

The Tri- π -Methane Rearrangement; Excited and Ground State VersionsMechanistic and Exploratory Organic Photochemistry¹

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SUPPLEMENTARY MATERIAL

Kinetics Derivations

$$dA/dt = -(k_1 + k_2)A$$

$$A = A_0 e^{-(k_1 + k_2)t}$$

$$dB/dt = k_1 A - k_3 B$$

$$dB/dt + k_3 B = k_1 A_0 e^{-(k_1 + k_2)t}$$

$$B = B_0 e^{-k_3 t} + (k_1 A_0) / (k_3 - k_1 - k_2) [e^{-(k_1 + k_2)t} - e^{-k_3 t}]$$

Note that these rate constants contain extinction coefficients as well as efficiencies of reaction

Derivatives:

For all data points at times t , get:

$$L(t) = e^{-(k_1 + k_2)t} - e^{-k_3 t}$$

$$M = k_1 / (k_3 - k_1 - k_2)$$

$$MK2 = k_1 / (k_3 - k_1 - k_2)^2$$

$$MK1 = (k_3 - k_2) / (k_3 - k_2 - k_1)^2$$

!Three derivatives of M w/r to the three rate constants k_1 , k_2 and k_3

$$MK3 = -MK2$$

$$B(t) = M L(t)$$

$$\text{Del}_B(t) = B(t) - BE(t) \quad \text{Where } BE(t) \text{ is the experimental } B \text{ at time } t$$

$$M = k_1 / (k_3 - k_1 - k_2)$$

$$MK2 = k_1 / (k_3 - k_1 - k_2)^2$$

$$MK1 = (k_3 - k_2) / (k_3 - k_2 - k_1)^2$$

$$MK3 = -MK2$$

$$L(t) = e^{-(k_1 + k_2)t} - e^{-k_3 t}$$

$$LK1(t) = -t e^{-(k_1 + k_2)t}$$

!Three derivatives of L w/r to the three rate constants k_1 , k_2 and k_3

S2

$$LK2(t) = LK1(t)$$

$$LK3(t) = te^{-k_3t}$$

$$B(t) = M[e^{-(k_1+k_2)t} - e^{-k_3t}]$$

$$\text{Del_B}(t) = B(t) - BE(t)$$

!Error Vector

$$BK1(t) = MK1 \cdot L(t) + M \cdot LK1(t)$$

!Three derivatives of B with respect to the three
! rate constants k_1 , k_2 and k_3

$$BK2(t) = MK2 \cdot L(t) + M \cdot LK2(t)$$

$$BK3(t) = MK3 \cdot L(t) + M \cdot LK3(t)$$

C—Set up Fmat

!Fmat is the matrix of partial derivatives of B(t)
!w/r to k_j with $r = 1, 2$ and 3 , resp. - r in
!columns and t in rows

Do t = 1, NData

$$FMat(t,1) = Bk1(t)$$

$$FMat(t,2) = Bk2(t)$$

$$FMat(t,3) = BK3(t)$$

Enddo

C—Now Transpose FMat to give TFMat

C—Now Pre-Multiply FMat by TFMat

C—Now Get TFFMat (TFFMat = TFMat*FMat)

C—Now Invert TFFMat

C—Multiply Inverse FFI * TFMat (i.e. Inverse of FFMat * Transpose of FFMat)

C—(i.e. TFMat) to give XMat

C—Get Del_K Vector: Pre-Multiply Del_B Vector by XMat

C—Calculate Square of Error Sum and Sum of Rate Const Abs Value Deviations

C—If not Converged, Get New Rate Constants and Recycle

$$K1 = K1 - \text{Del_K}(1)$$

$$K2 = K2 - \text{Del_K}(2)$$

$$K3 = K3 - \text{Del_K}(3)$$

Flow Diagram for ABC_Kinetics Fortran Programming

C—Get File Name

C—Strip off Any Extension Present

Call Strip_Name(FileIn,FName,ILen)

C—Possible Data Input File

C—Open the Data Input File

Call Open_File(DFile,Nunit,Ext,IO,IOK)

!Open Input File

C—Possible Data Output File

C—Open the Data Output File

Call Open_File(DFile,Nunit,Ext,IO,IOK)

!Open Data Output

C—Possible Debugging Output File

C—Open the IBUG Output File

Call Open_File(FName,Nunit,Ext,IO,IOK)

!Open .DBG File

C—Get New Kin Vec File to be Output

C—Now do actual open of new .KIN Kin_Unit file to be output

S3

Call Open_File(FName,Nunit,Ext,IO,IOK) !Open Output .KIN Result File
 C—Get an Error Limit (followed by other initial parameters)
 Call Floater(Err,Err_Lim,Ierr_Flg) !character in & floating out
 C—Get a Damping Factor
 Call Floater(Damper,Damp,Ierr_Flg) !character in & floating out
 C—Get the Assumed Rate Constants in Floating Pt, Fk1, Fk2, Fk3
 C—Ao is taken as 1.0, Bo as zero
 Call Floater(Const,Fk1,Ierr_Flg) !Floating pt output
 Call Floater(Const,Fk2,Ierr_Flg) !Floating pt output
 Call Floater(Const,Fk3,Ierr_Flg) !Floating pt output
 C—Error Trap for Fk3-Fk1-Fk2 being equal to zero
 C—Manual Input; Give the Time for Each Measurement and the Amount of B
 C—To Next Entry
 C—File Input; Input this Data
 C—Get Each Del_Bvec from the Entered BEVec(i) and the Calculated BVec(i)
 C—Use Damping for this point
 C—Prepare for Main Loop
 C—Now Calculate Theoretical Functions
 C—Main Loop
 C—Check for Acceptable Input Initial Parameters
 C—Choice of Input Parameters is All Right
 C—Set up Fmat
 Call PrintMat(FMat,Tot_Cols,Tot_Rows,Col_per_Row)
 C—Now Transpose FMat to give TFMat
 Call Transpos(FMat,TFMat,mm,nn)
 Call PrintMat(TFMat,Tot_Cols,Tot_Rows,Col_per_Row)
 C—Now Get TFFMat (TFFMat = TFMat*FMat)
 Call Mul_Mat(TFMat,FMat,TFFMat,n1,n2,n3)
 Call PrintMat(TFFMat,Tot_Cols,Tot_Rows,Col_per_Row)
 C—Now Invert TFFMat
 Call MatInv(TFFMat,NSiz,Determ)
 C—Now Print Out the Inverse of TFF (i.e. FFIMat)
 Call PrintMat(FFIMat,Tot_Cols,Tot_Rows,Col_per_Row)
 C—Multiply Inverse FFI * TFMat (i.e. Inverse of FFIMat * Transpose of FFIMat)
 Call Mul_Mat(FFIMat,TFMat,XMat,n1,n2,n3) !Multiply Inverse * Transpose of
 C—Now Print Out the Product XMat = FFIMat * TFMat)
 Call PrintMat(XMat,Tot_Cols,Tot_Rows,Col_per_Row)
 C—Get Del_K Vector
 Call Mul_Mat(XMat,Del_BVec,Del_K,n1,n2,n3)
 C—Damp Del_K to Smaller Values
 C—Write Out Del_K in Column Format
 C—Calculate Square of Error Sum and Sum of Rate Const Abs Value Deviations
 C—Format Error, Large Number Output
 C—Converged; Print the Final BVec,BEVec and Del_BVec Listing
 C—Close Files
 C—Convert String to Capitals
 C—Subroutine PrintMat
 Subroutine PrintMat(Matrix,Tot_Cols,Tot_Rows,Col_per_Row)
 C—This subroutine prints out matrices
 C—Level of Printing
 C—Write Column Numbering (Headers)
 C—Write Dashes for the Columns
 C—Write Row Numbering (Headers) and Put in Floating Point Values
 C—Function Lens
 Subroutine Open_File(FName,NUnit,Ext,IO,IOK)
 C—Input Case (Read)
 Subroutine Strip_Name(FileIn,FName,ILen)
 C—Subroutine to Multiply Two Matrices
 Subroutine Mul_Mat(Matrix1,Matrix2,Matrix3,n1,n2,n3)
 C—Matrix1(n1,n2), Matrix2(n2,n3), Matrix3(n1,n3)
 C
 C Subroutine to Transpose a Matrix
 C
 C Subroutine Transpos(FMAT,TFMat,mm,nn)

C _____
C Subroutine to Transpose a Matrix
C _____
C—Take Transpose

If(IScreen.eq.1)Write(Tunit,*)'In Transpose Subroutine'
Write(Bunit,*)'In Transpose Subroutine'

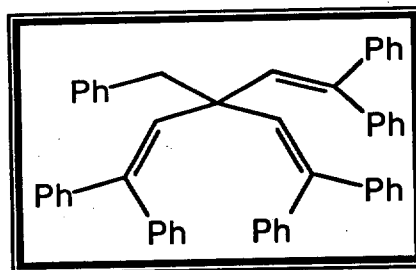
C—Invert, A Matrix Inversion Subroutine
Subroutine Matinv (A,N,D)

C—Subroutine to Check for Proper Floating Point Input
Subroutine Floater(Char_Input,Float_Out,Ierr_Flg)

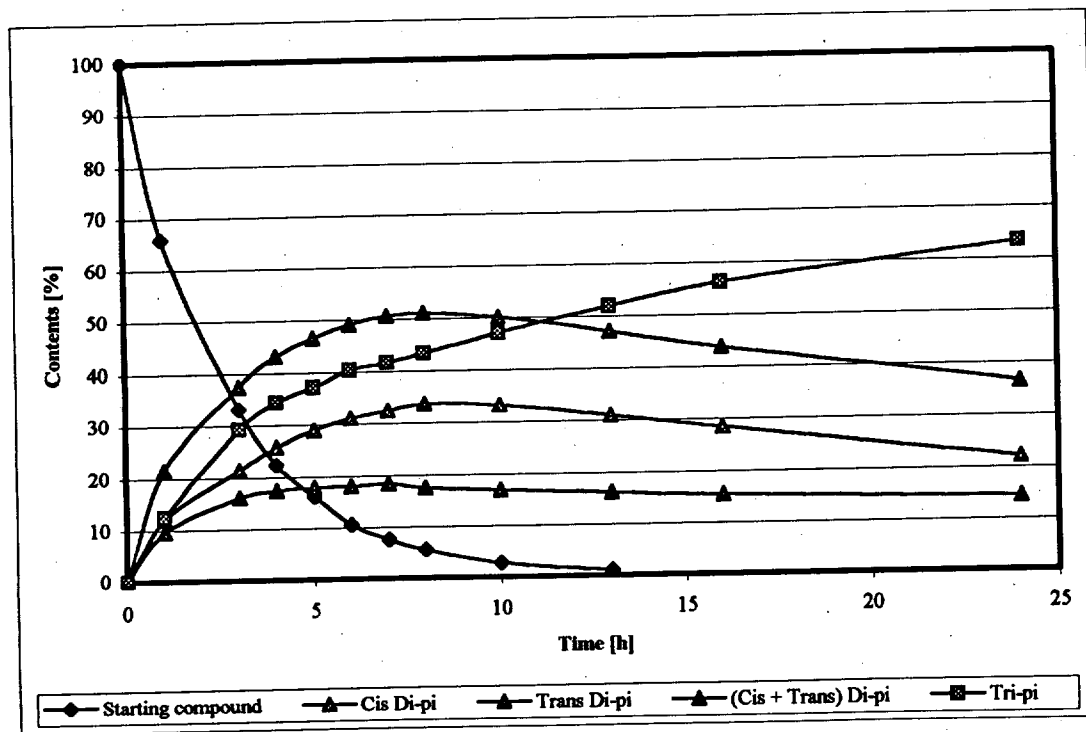
Data for Kinetics with Concentrations Versus Time

Graph-Benzyl-Direct Data:

Starting	Cis Di- π	Trans Di- π	Σ Di- π	Tri- π
100	0	0	0	0
65.95	12.03	9.56	21.59	12.46
33.22	21.43	16.11	37.54	29.24
22.41	25.73	17.44	43.17	34.42
16.13	28.81	17.85	46.66	37.21
10.61	31.08	17.97	49.05	40.34
7.66	32.37	18.32	50.69	41.65
5.49	33.66	17.48	51.14	43.37
2.68	33.29	16.94	50.23	47.09
0.94	30.94	16.14	47.08	51.98
	28.33	15.43	43.76	56.24
	22.11	14.37	36.48	63.52

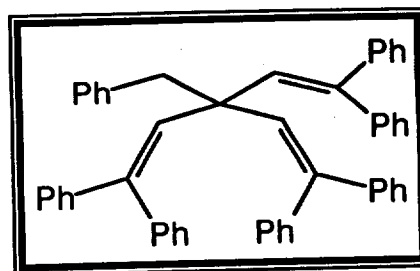


$K1 = 0.2226$ $K2 = 0.1433$ $K3 = 0.0242$



Graph-Benzyl-Naphthalene Sensitized Data:

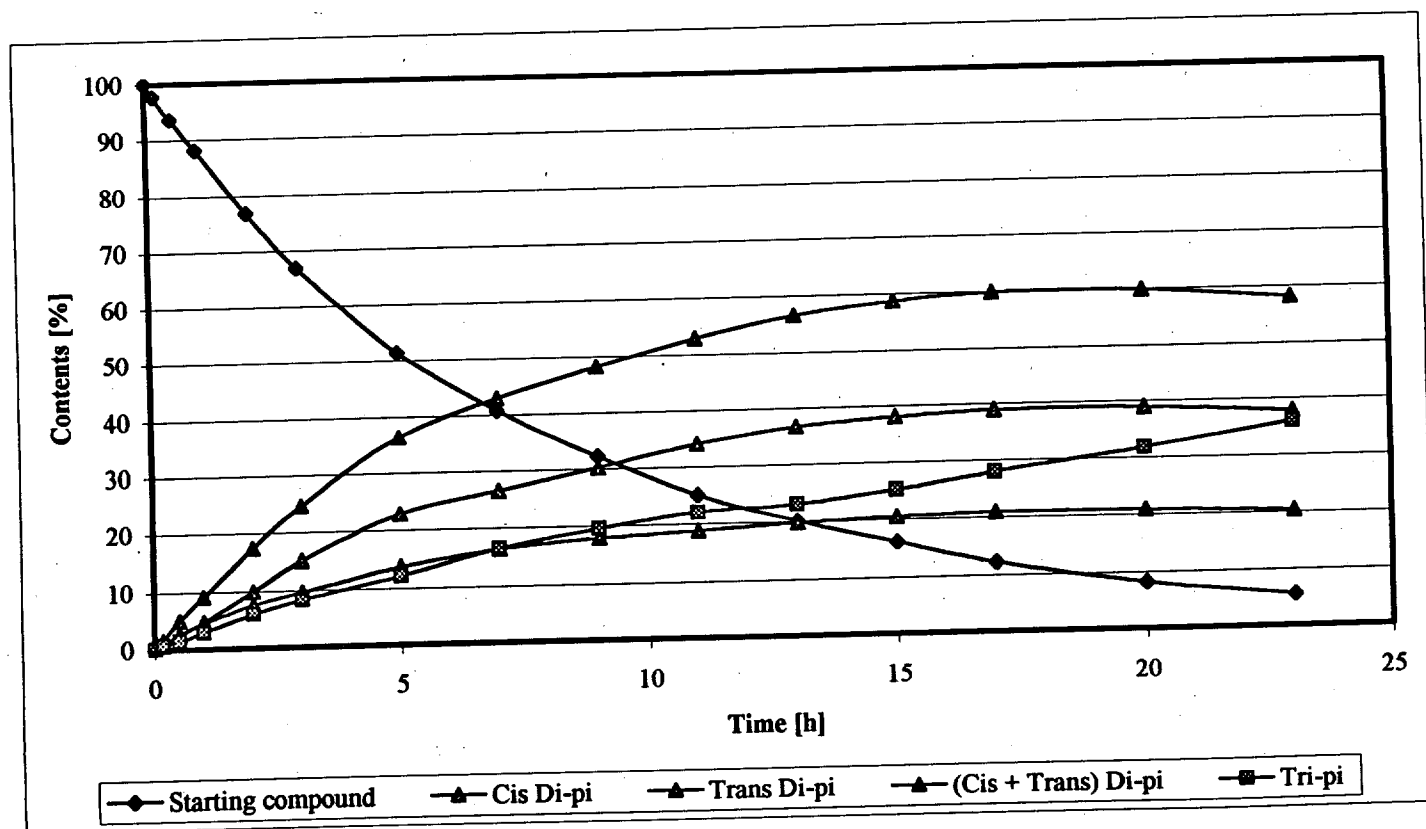
Time [h]	Starting	Cis Di- π	Trans Di- π	Σ Di- π	Tri- π
0	100	0	0	0	0
0.17	97.85	0.72	0.71	1.43	0.72
0.5	93.81	2.44	2.43	4.87	1.32
1	88.15	4.63	4.38	9.01	2.84
2	76.83	9.89	7.43	17.32	5.85
3	66.98	15.07	9.64	24.71	8.31
5	51.52	22.82	13.54	36.36	12.12
7	40.77	26.57	16.28	42.85	16.38
9	32.33	30.28	17.84	48.12	19.55
11	25.11	34.04	18.82	52.86	22.03
13	20.15	36.76	19.79	56.55	23.12
15	16.04	38.12	20.53	58.65	25.31
17	12.12	38.96	20.98	59.94	27.94
20	8.25	38.96	20.96	59.92	31.83
23	5.62	37.88	20.35	58.23	36.15



K1 = 0.0988

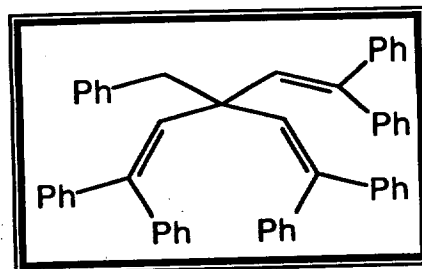
K2 = 0.0281

K3 = 0.0139



Graph-Benzyl-Acetophenone Sensitized Data:

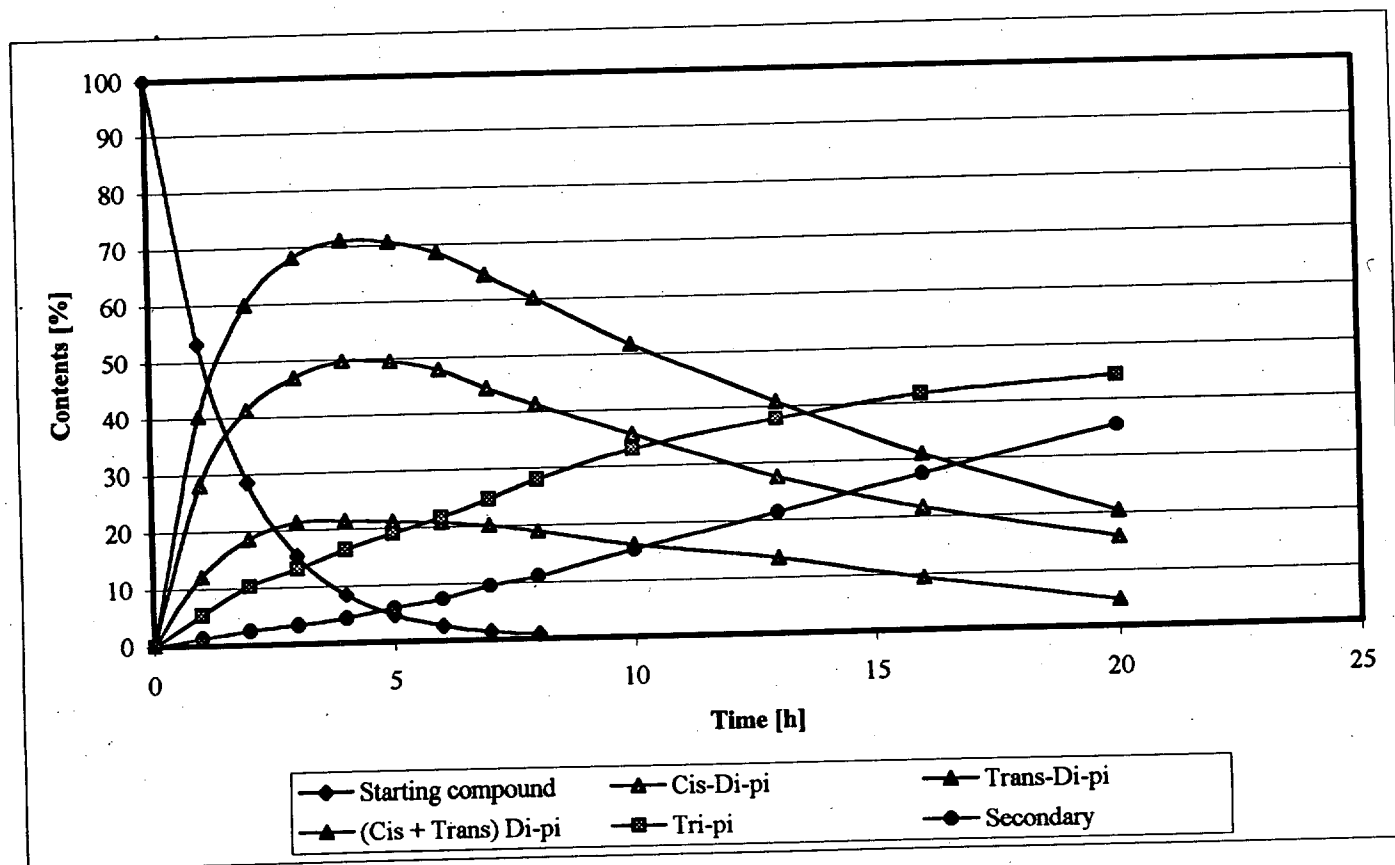
Time [h]	Starting	Cis Di- π	Trans Di- π	Σ Di- π	Tri- π	Secondary
0	100	0	0	0	0	0
1	53.28	28.15	12.13	40.28	5.22	1.22
2	28.48	41.33	18.55	59.88	10.29	2.35
3	15.49	46.8	21.35	68.15	13.22	3.14
4	8.32	49.64	21.45	71.09	16.36	4.23
5	4.53	49.48	21.13	70.61	19.04	5.82
6	2.44	47.71	20.84	68.55	21.72	7.29
7	1.32	44.23	20.16	64.39	24.82	9.47
8	0.81	41.24	18.87	60.11	27.96	11.12
10		35.47	16.21	51.68	32.93	15.39
13		27.51	13.35	40.86	37.73	21.41
16		21.66	9.23	30.89	41.63	27.48
20		15.69	4.62	20.31	44.22	35.37



$$K1 = 0.5573$$

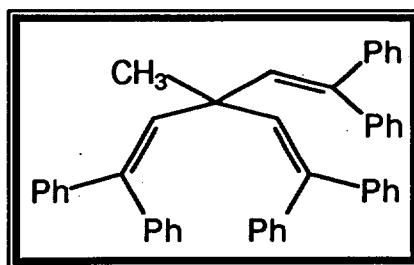
$$K2 = 0.0677$$

$$K3 = 0.0525$$



Graph-Methyl-Direct Data:

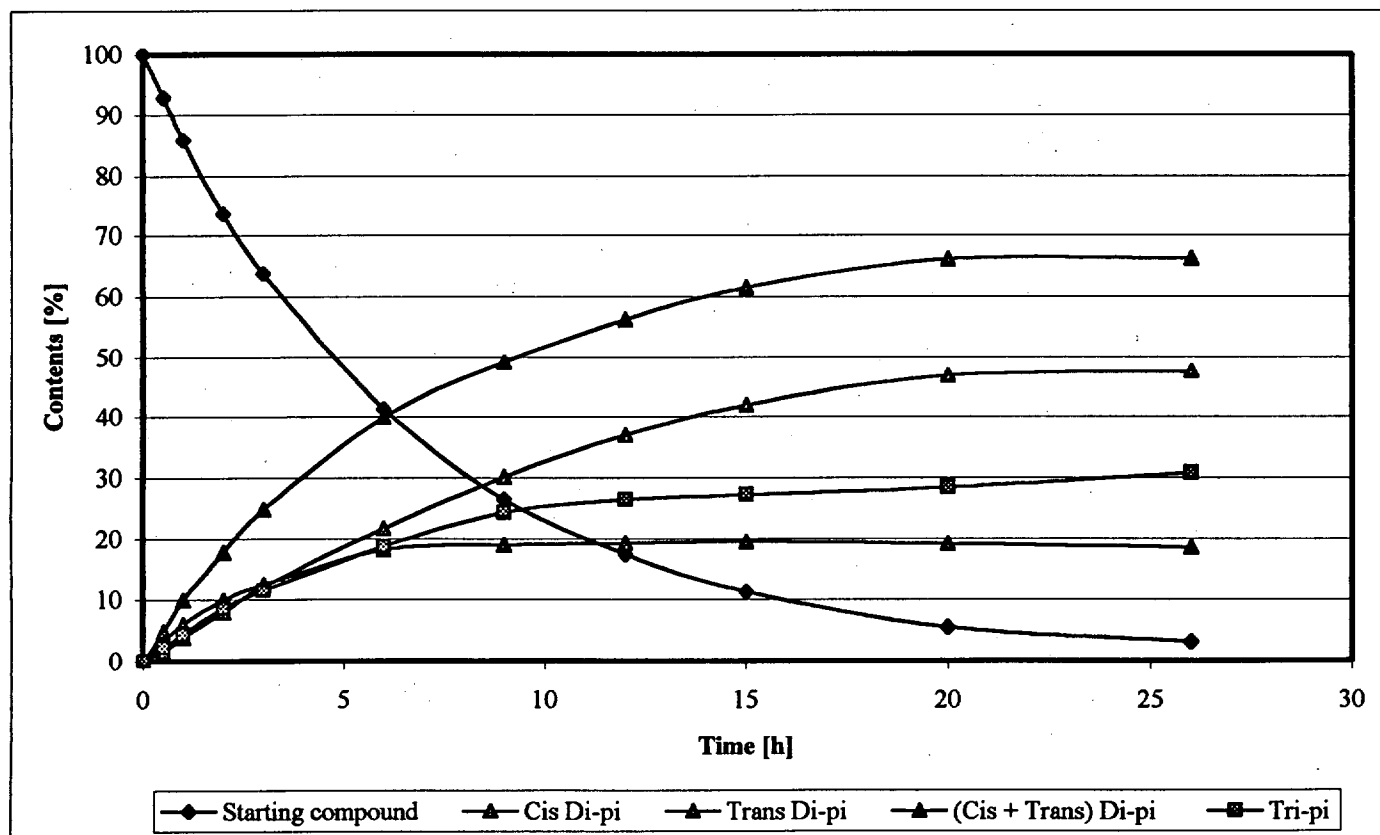
Time [h]	Starting	Cis Di- π	Trans Di- π	Σ Di- π	Tri-pi
0	100	0	0	0	0
0.5	92.84	1.66	3.23	4.89	2.27
1	85.75	3.89	5.97	9.86	4.39
2	73.55	7.91	9.86	17.77	8.68
3	63.71	12.23	12.59	24.82	11.47
6	41.31	21.71	18.22	39.93	18.76
9	26.58	30.11	19.02	49.13	24.29
12	17.47	36.86	19.26	56.12	26.41
15	11.25	41.96	19.48	61.44	27.31
20	5.48	46.83	19.21	66.04	28.48
26	3.11	47.57	18.57	66.14	30.75



K1 = 0.1016

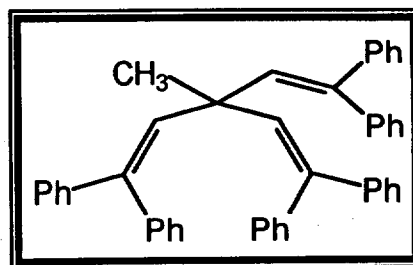
K2 = 0.0448

K3 = 0.0006



Graph-Methyl-Naphthalene-Sensitized Data:

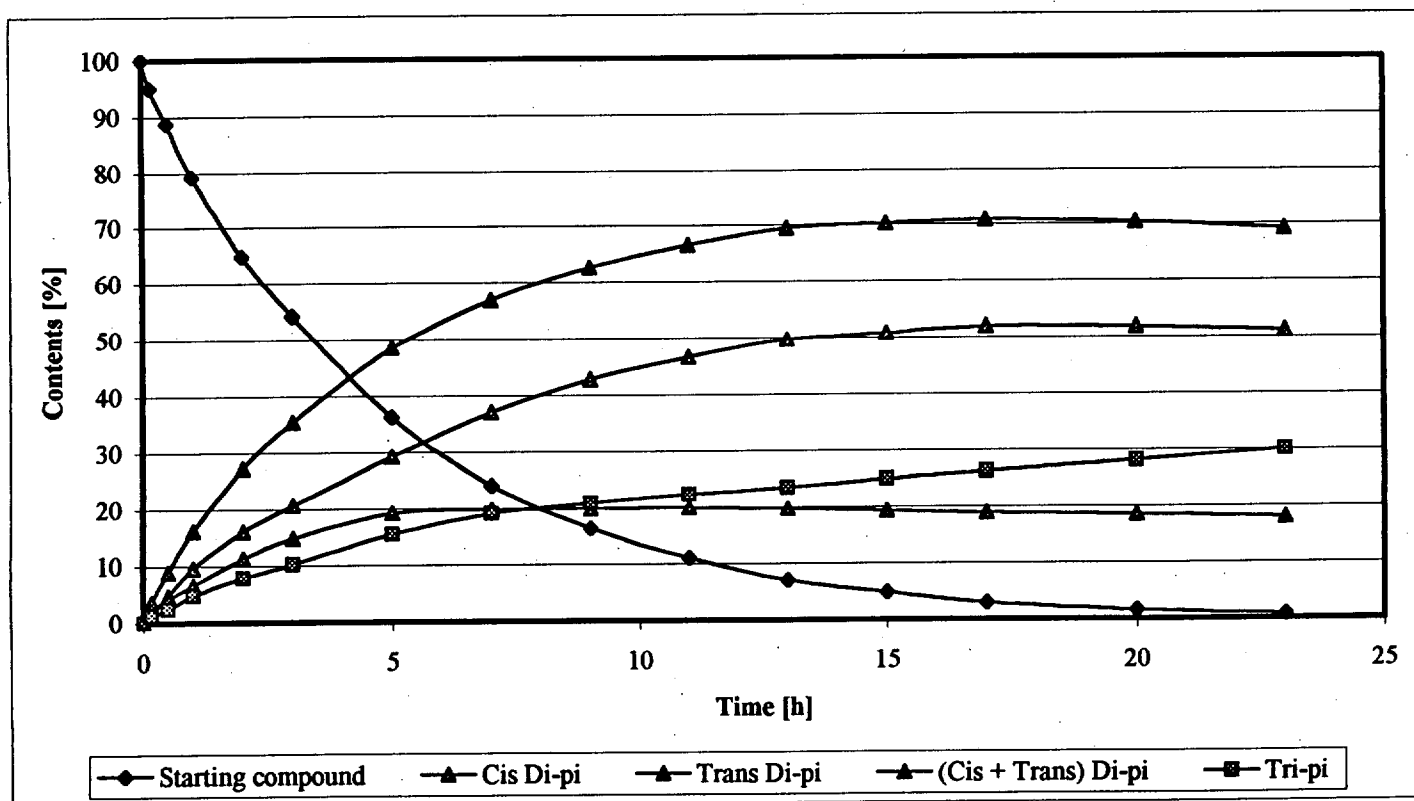
Time [h]	Starting	Cis Di- π	Trans Di- π	Σ Di- π	Tri-pi
0	100	0	0	0	0
0.17	95.09	1.79	1.88	3.67	1.24
0.5	88.75	4.76	4.12	8.88	2.37
1	79.16	9.55	6.54	16.09	4.75
2	64.94	16.03	11.24	27.27	7.79
3	54.25	20.68	14.81	35.49	10.26
5	36.21	29.16	19.22	48.38	15.41
7	24.09	37.09	19.78	56.87	19.04
9	16.42	42.78	19.89	62.67	20.91
11	11.03	46.58	19.98	66.56	22.41
13	7.08	49.64	19.75	69.39	23.53
15	4.86	50.85	19.34	70.19	24.95
17	2.96	51.88	18.89	70.77	26.27
20	1.54	51.87	18.47	70.34	28.12
23	0.84	51.13	18.01	69.14	30.02



K1 = 0.1628

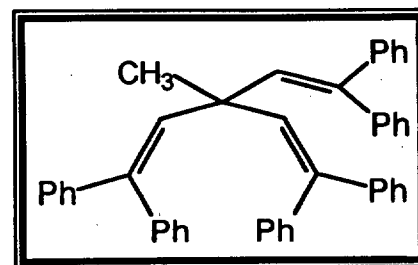
K2 = 0.0528

K3 = 0.0038



Graph-Methyl-Acetophenone Sensitized Data:

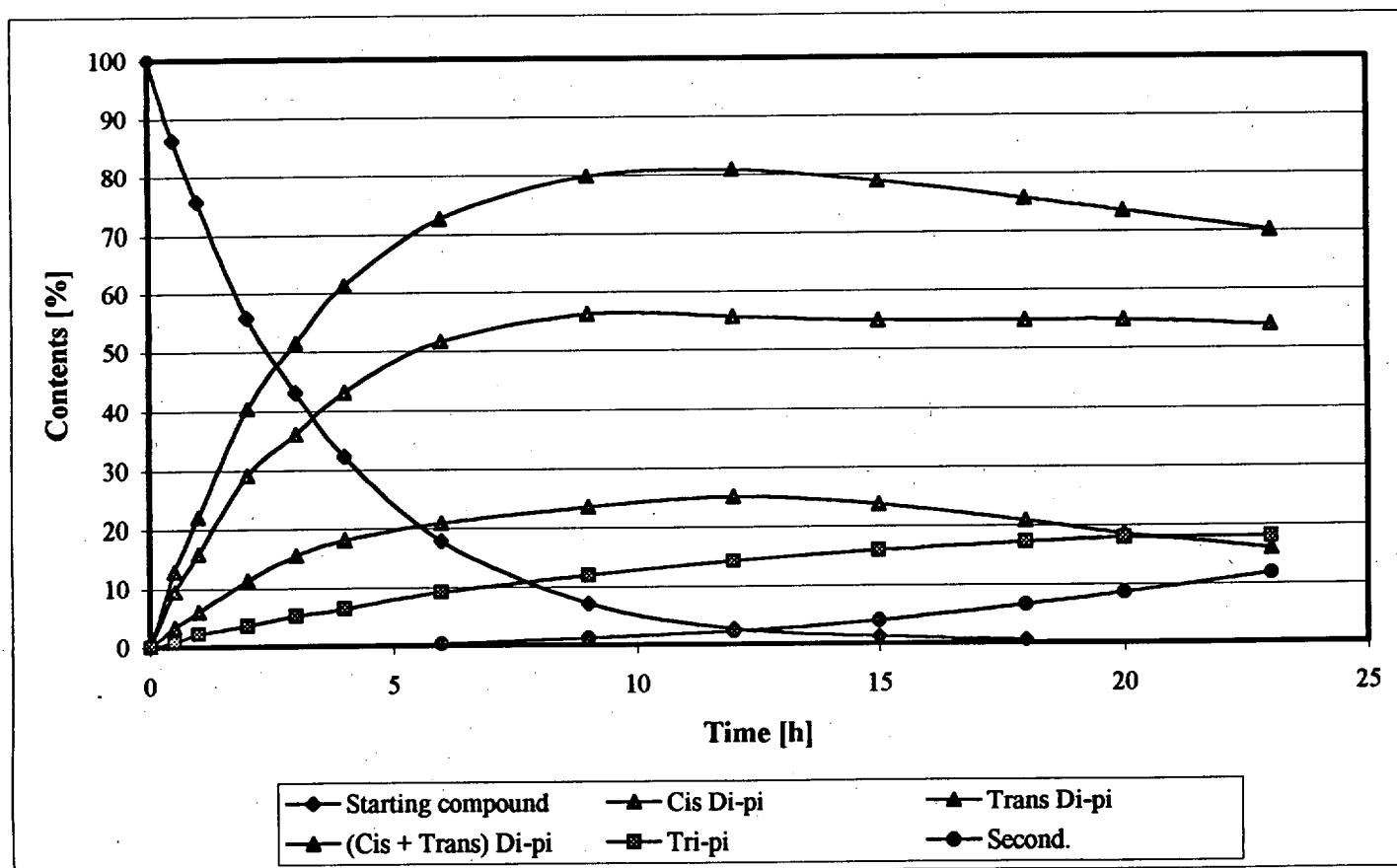
Time [h]	Starting	Cis Di- π	Trans Di- π	Σ Di- π	Tri- π	Secondary
0	100	0	0	0	0	
0.5	86.21	9.48	3.45	12.93	0.86	
1	75.76	15.91	6.06	21.97	2.27	
2	55.91	29.1	11.29	40.39	3.7	
3	43.21	36.01	15.53	51.54	5.25	
4	32.22	43.22	18.15	61.37	6.41	
6	17.98	51.69	20.88	72.57	9.13	0.32
9	7.09	56.28	23.53	79.81	11.95	1.15
12	2.66	55.7	25.14	80.84	14.27	2.23
15	1.25	55.03	23.71	78.74	16.04	3.97
18	0.53	54.84	20.82	75.66	17.26	6.55
20		54.86	18.62	73.48	17.94	8.58
23		54	16.11	70.11	18.04	11.85



K1 = 0.2591

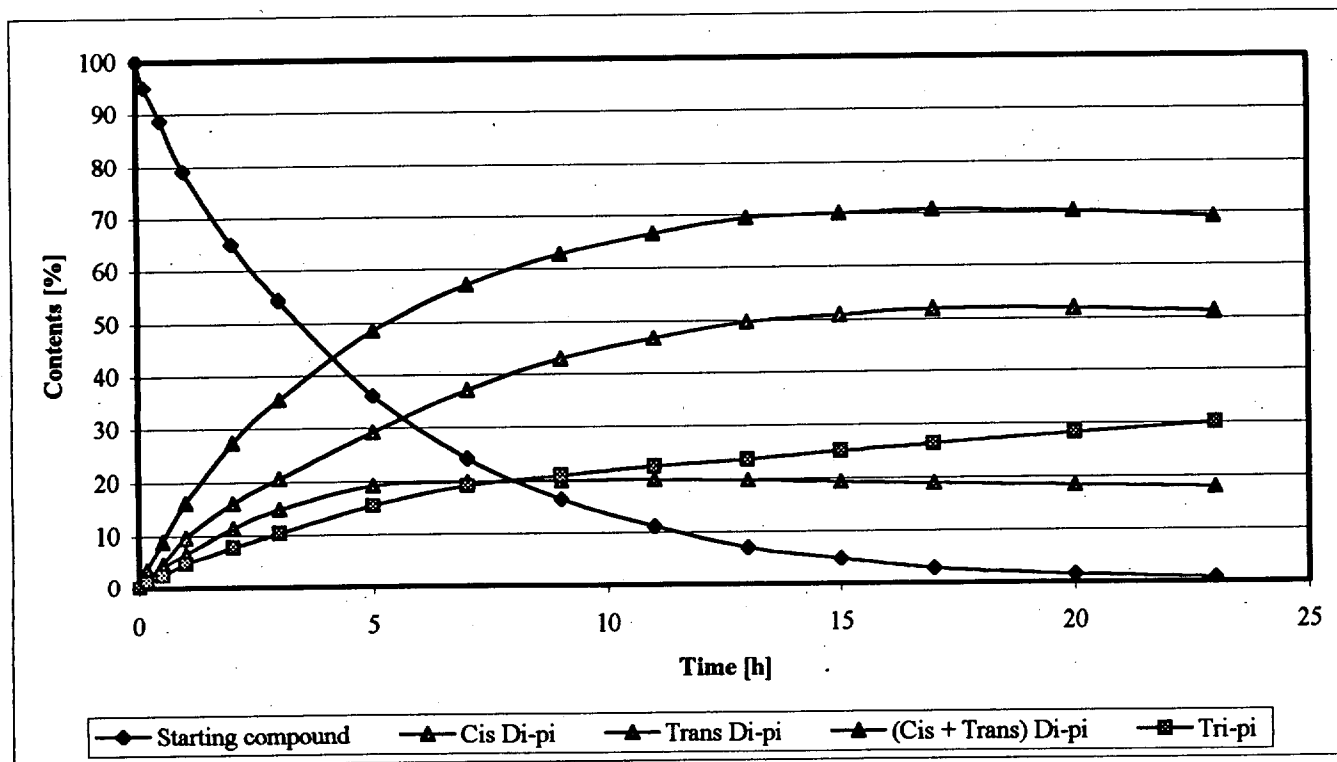
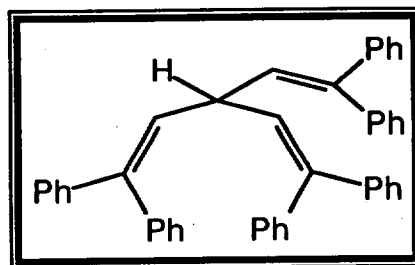
K2 = 0.0077

K3 = 0.0170



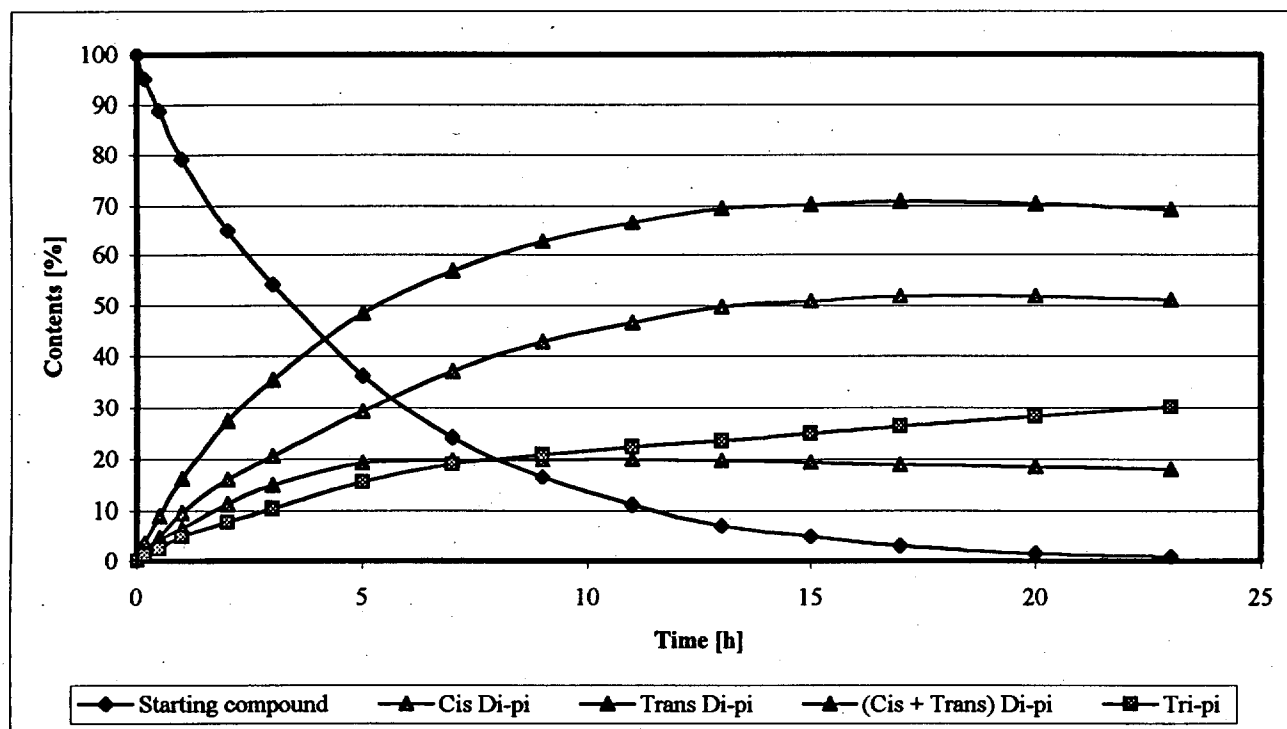
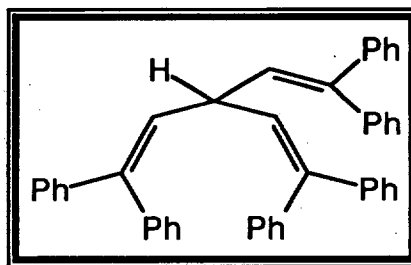
Graph-Hydrogen Direct

Time [h]	Starting	Cis Di- π	Trans Di- π	Σ Di- π
0	100	0	0	0
1	98.08	1.16	0.76	1.92
2	96.22	2.07	1.71	3.78
4	93.05	4.24	2.71	6.95
6	89.76	6.09	4.15	10.24
12	80.42	12.77	6.81	19.58
18	72.48	18.38	9.14	27.52
24	65.11	24.38	10.51	34.89
30	58.14	29.88	11.98	41.86
36	52.83	33.79	13.38	47.17
42	47.22	38.47	14.31	52.78
48	43.24	41.82	14.94	56.76
54	38.55	45.52	15.93	61.45
60	34.39	48.87	16.74	65.61
66	30.42	51.63	17.95	69.58



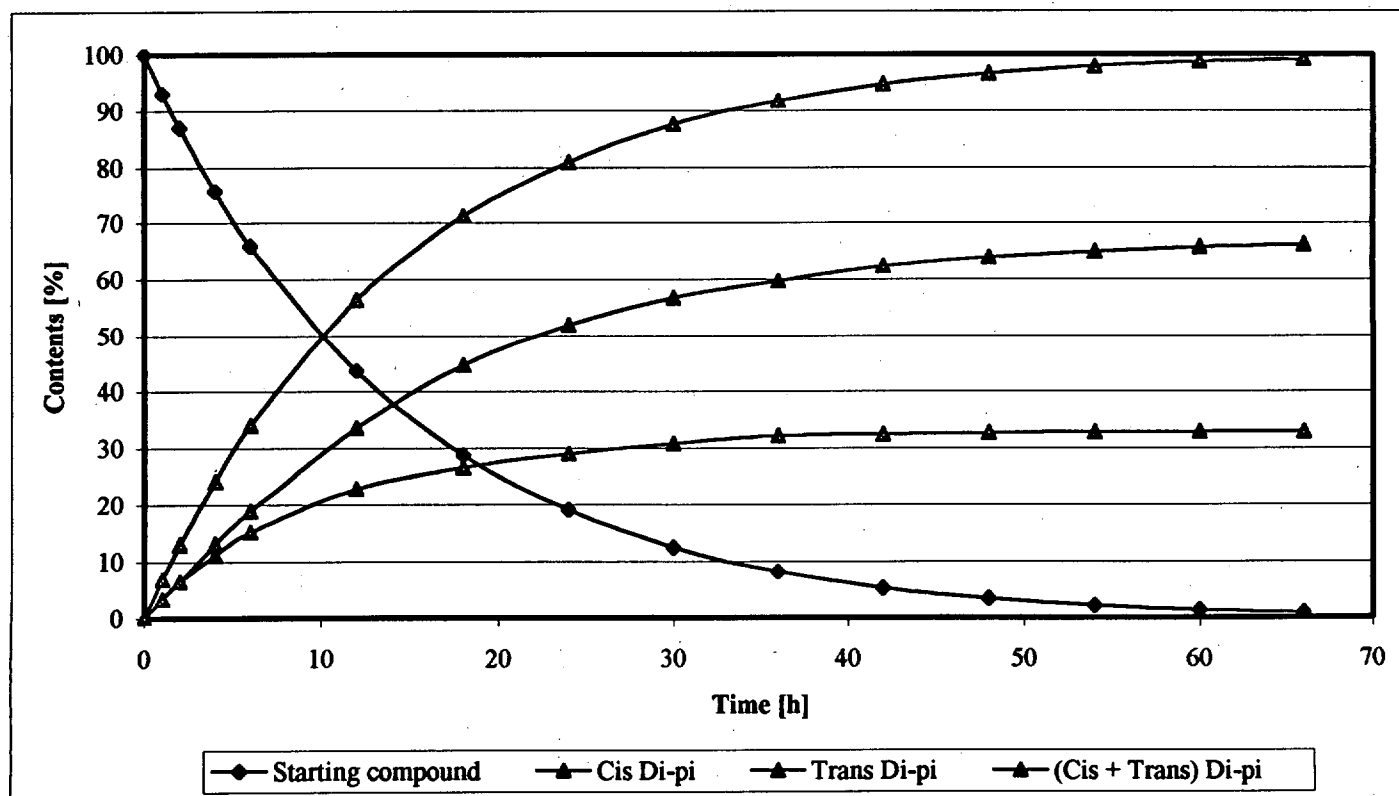
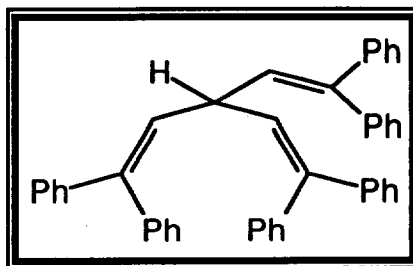
Graph-Hydrogen Naphthalene Sensitized

Time [h]	Starting	Cis Di- π	Trans Di- π	Σ Di- π
0	100	0	0	0
0.5	93.66	3.75	2.59	6.34
1	88.18	7.14	4.68	11.82
2	80.77	12.12	7.11	19.23
3	74.05	16.03	9.92	25.95
5	61.88	24.75	13.37	38.12
7	49.88	34.46	15.66	50.12
9	40.75	41.46	17.79	59.25
11	33.39	47.96	18.65	66.61
13	27.21	53.68	19.11	72.79
15	22.38	58.19	19.43	77.62
17	18.19	62.16	19.65	81.81
20	13.32	66.91	19.77	86.68
23	9.87	70.27	19.86	90.13
29	5.13	74.95	19.92	94.87



Graph-Hydrogen Acetophenone Sensitized

Time [h]	Starting	Cis Di- π	Trans Di- π	Σ Di- π
0	100	0	0	0
1	93.22	3.39	3.39	6.78
2	87.08	6.46	6.46	12.92
4	75.77	13.12	11.11	24.23
6	66.04	18.88	15.08	33.96
12	43.58	33.57	22.85	56.42
18	28.79	44.65	26.56	71.21
24	19.11	51.96	28.93	80.89
30	12.44	56.75	30.81	87.56
36	8.14	59.71	32.15	91.86
42	5.24	62.37	32.39	94.76
48	3.38	63.96	32.66	96.62
54	2.19	65.05	32.76	97.81
60	1.42	65.77	32.81	98.58
66	0.94	66.21	32.85	99.06



Kinetic Runs Iterative Solutions

Note: Rate Constants k_1 , k_2 and k_3 in the first three columns and the error in the deviation of the B concentration as the last column

Benzyl-Direct as Representative

Damping Factor is 0.050000000

Initial Rate Constants Given

fk1,fk2,fk3 0.100000 0.100000 0.100000

NData,Err_Lim 12 0.000001

Vlad-Bz-D.Kin R = Methyl, Direct Irradiation

Cycle 1*	New Rate Constants & Err_K:	0.106146	0.122643	0.080176	0.048613	Cycle 93*	New Rate Constants & Err_K:	0.222127	0.143498	0.024283	0.000089
Cycle 2*	New Rate Constants & Err_K:	0.111937	0.134189	0.070268	0.027246	Cycle 94*	New Rate Constants & Err_K:	0.222183	0.143477	0.024275	0.000084
Cycle 3*	New Rate Constants & Err_K:	0.117428	0.141876	0.063470	0.019975	Cycle 95*	New Rate Constants & Err_K:	0.222235	0.143457	0.024267	0.000080
Cycle 4*	New Rate Constants & Err_K:	0.122640	0.147330	0.058361	0.015775	Cycle 96*	New Rate Constants & Err_K:	0.222286	0.143438	0.024260	0.000076
Cycle 5*	New Rate Constants & Err_K:	0.127591	0.151301	0.054329	0.012954	Cycle 97*	New Rate Constants & Err_K:	0.222333	0.143421	0.024253	0.000072
Cycle 6*	New Rate Constants & Err_K:	0.132296	0.154218	0.051044	0.010907	Cycle 98*	New Rate Constants & Err_K:	0.222379	0.143404	0.024246	0.000069
Cycle 7*	New Rate Constants & Err_K:	0.136769	0.156357	0.048308	0.009348	Cycle 99*	New Rate Constants & Err_K:	0.222422	0.143388	0.024240	0.000065
Cycle 8*	New Rate Constants & Err_K:	0.141020	0.157905	0.045988	0.008119	Cycle 100*	New Rate Constants & Err_K:	0.222463	0.143373	0.024234	0.000062
Cycle 9*	New Rate Constants & Err_K:	0.145063	0.158999	0.043996	0.007128	Cycle 101*	New Rate Constants & Err_K:	0.222502	0.143359	0.024228	0.000059
Cycle 10*	New Rate Constants & Err_K:	0.148906	0.159736	0.042265	0.006312	Cycle 102*	New Rate Constants & Err_K:	0.222539	0.143345	0.024223	0.000056
Cycle 11*	New Rate Constants & Err_K:	0.152560	0.160194	0.040748	0.005630	Cycle 103*	New Rate Constants & Err_K:	0.222574	0.143333	0.024218	0.000053
Cycle 12*	New Rate Constants & Err_K:	0.156035	0.160431	0.039408	0.005052	Cycle 104*	New Rate Constants & Err_K:	0.222608	0.143321	0.024213	0.000050
Cycle 13*	New Rate Constants & Err_K:	0.159339	0.160493	0.038216	0.004558	Cycle 105*	New Rate Constants & Err_K:	0.222640	0.143309	0.024208	0.000048
Cycle 14*	New Rate Constants & Err_K:	0.162481	0.160416	0.037150	0.004285	Cycle 106*	New Rate Constants & Err_K:	0.222670	0.143298	0.024204	0.000046
Cycle 15*	New Rate Constants & Err_K:	0.165469	0.160229	0.036191	0.004133	Cycle 107*	New Rate Constants & Err_K:	0.222699	0.143288	0.024200	0.000043
Cycle 16*	New Rate Constants & Err_K:	0.168310	0.159956	0.035326	0.003980	Cycle 108*	New Rate Constants & Err_K:	0.222726	0.143278	0.024196	0.000041
Cycle 17*	New Rate Constants & Err_K:	0.171011	0.159616	0.034541	0.003826	Cycle 109*	New Rate Constants & Err_K:	0.222753	0.143269	0.024192	0.000039
Cycle 18*	New Rate Constants & Err_K:	0.173580	0.159224	0.033827	0.003675	Cycle 110*	New Rate Constants & Err_K:	0.222777	0.143261	0.024188	0.000037
Cycle 19*	New Rate Constants & Err_K:	0.176023	0.158793	0.033175	0.003526	Cycle 111*	New Rate Constants & Err_K:	0.222801	0.143252	0.024185	0.000035
Cycle 20*	New Rate Constants & Err_K:	0.178346	0.158333	0.032578	0.003379	Cycle 112*	New Rate Constants & Err_K:	0.222823	0.143245	0.024182	0.000033
Cycle 21*	New Rate Constants & Err_K:	0.180554	0.157853	0.032030	0.003236	Cycle 113*	New Rate Constants & Err_K:	0.222845	0.143237	0.024179	0.000032
Cycle 22*	New Rate Constants & Err_K:	0.182654	0.157360	0.031526	0.003097	Cycle 114*	New Rate Constants & Err_K:	0.222865	0.143230	0.024176	0.000030
Cycle 23*	New Rate Constants & Err_K:	0.184651	0.156860	0.031061	0.002962	Cycle 115*	New Rate Constants & Err_K:	0.222884	0.143224	0.024173	0.000029
Cycle 24*	New Rate Constants & Err_K:	0.186550	0.156356	0.030631	0.002832	Cycle 116*	New Rate Constants & Err_K:	0.222903	0.143217	0.024170	0.000027
Cycle 25*	New Rate Constants & Err_K:	0.188356	0.155854	0.030234	0.002706	Cycle 117*	New Rate Constants & Err_K:	0.222920	0.143212	0.024168	0.000026
Cycle 26*	New Rate Constants & Err_K:	0.190073	0.155356	0.029865	0.002584	Cycle 118*	New Rate Constants & Err_K:	0.222937	0.143206	0.024165	0.000025
Cycle 27*	New Rate Constants & Err_K:	0.191705	0.154864	0.029522	0.002467	Cycle 119*	New Rate Constants & Err_K:	0.222952	0.143201	0.024163	0.000023
Cycle 28*	New Rate Constants & Err_K:	0.193257	0.154381	0.029204	0.002354	Cycle 120*	New Rate Constants & Err_K:	0.222967	0.143196	0.024161	0.000022
Cycle 29*	New Rate Constants & Err_K:	0.194733	0.153909	0.028907	0.002245	Cycle 121*	New Rate Constants & Err_K:	0.222982	0.143191	0.024159	0.000021
Cycle 30*	New Rate Constants & Err_K:	0.196137	0.153447	0.028630	0.002141	Cycle 122*	New Rate Constants & Err_K:	0.222995	0.143187	0.024157	0.000020
Cycle 31*	New Rate Constants & Err_K:	0.197471	0.152999	0.028372	0.002042	Cycle 123*	New Rate Constants & Err_K:	0.223008	0.143182	0.024155	0.000019
Cycle 32*	New Rate Constants & Err_K:	0.198740	0.152563	0.028130	0.001946	Cycle 124*	New Rate Constants & Err_K:	0.223020	0.143178	0.024153	0.000018
Cycle 33*	New Rate Constants & Err_K:	0.199946	0.152141	0.027904	0.001854	Cycle 125*	New Rate Constants & Err_K:	0.223032	0.143175	0.024151	0.000017
Cycle 34*	New Rate Constants & Err_K:	0.201093	0.151733	0.027692	0.001767	Cycle 126*	New Rate Constants & Err_K:	0.223043	0.143171	0.024150	0.000016
Cycle 35*	New Rate Constants & Err_K:	0.202184	0.151339	0.027494	0.001683	Cycle 127*	New Rate Constants & Err_K:	0.223054	0.143168	0.024148	0.000015
Cycle 36*	New Rate Constants & Err_K:	0.203221	0.150960	0.027308	0.001603	Cycle 128*	New Rate Constants & Err_K:	0.223064	0.143165	0.024147	0.000015
Cycle 37*	New Rate Constants & Err_K:	0.204207	0.150594	0.027133	0.001526	Cycle 129*	New Rate Constants & Err_K:	0.223073	0.143162	0.024145	0.000014
Cycle 38*	New Rate Constants & Err_K:	0.205144	0.150243	0.026969	0.001453	Cycle 130*	New Rate Constants & Err_K:	0.223082	0.143159	0.024144	0.000013
Cycle 39*	New Rate Constants & Err_K:	0.206035	0.149906	0.026814	0.001383	Cycle 131*	New Rate Constants & Err_K:	0.223091	0.143156	0.024143	0.000013
Cycle 40*	New Rate Constants & Err_K:	0.206883	0.149582	0.026669	0.001316	Cycle 132*	New Rate Constants & Err_K:	0.223099	0.143153	0.024142	0.000012
Cycle 41*	New Rate Constants & Err_K:	0.207689	0.149271	0.026533	0.001253	Cycle 133*	New Rate Constants & Err_K:	0.223107	0.143151	0.024140	0.000011
Cycle 42*	New Rate Constants & Err_K:	0.208455	0.148974	0.026404	0.001192	Cycle 134*	New Rate Constants & Err_K:	0.223114	0.143149	0.024139	0.000011
Cycle 43*	New Rate Constants & Err_K:	0.209183	0.148690	0.026282	0.001134	Cycle 135*	New Rate Constants & Err_K:	0.223121	0.143147	0.024138	0.000010
Cycle 44*	New Rate Constants & Err_K:	0.209876	0.148417	0.026168	0.001079	Cycle 136*	New Rate Constants & Err_K:	0.223128	0.143145	0.024137	0.000010
Cycle 45*	New Rate Constants & Err_K:	0.210534	0.148157	0.026060	0.001027	Cycle 137*	New Rate Constants & Err_K:	0.223134	0.143143	0.024136	0.000009
Cycle 46*	New Rate Constants & Err_K:	0.211160	0.147908	0.025958	0.000977	Cycle 138*	New Rate Constants & Err_K:	0.223140	0.143141	0.024136	0.000009
Cycle 47*	New Rate Constants & Err_K:	0.211756	0.147671	0.025862	0.000929	Cycle 139*	New Rate Constants & Err_K:	0.223146	0.143139	0.024135	0.000008
Cycle 48*	New Rate Constants & Err_K:	0.212322	0.147444	0.025771	0.000883	Cycle 140*	New Rate Constants & Err_K:	0.223152	0.143137	0.024134	0.000008
Cycle 49*	New Rate Constants & Err_K:	0.212860	0.147228	0.025686	0.000840	Cycle 141*	New Rate Constants & Err_K:	0.223157	0.143136	0.024133	0.000007
Cycle 50*	New Rate Constants & Err_K:	0.213371	0.147022	0.025604	0.000799	Cycle 142*	New Rate Constants & Err_K:	0.223162	0.143135	0.024132	0.000007
Cycle 51*	New Rate Constants & Err_K:	0.213858	0.146826	0.025528	0.000760	Cycle 143*	New Rate Constants & Err_K:	0.223166	0.143133	0.024132	0.000007
Cycle 52*	New Rate Constants & Err_K:	0.214320	0.146638	0.025455	0.000722	Cycle 144*	New Rate Constants & Err_K:	0.223171	0.143132	0.024131	0.000006
Cycle 53*	New Rate Constants & Err_K:	0.214760	0.146460	0.025387	0.000687	Cycle 145*	New Rate Constants & Err_K:	0.223175	0.143131	0.024130	0.000006
Cycle 54*	New Rate Constants & Err_K:	0.215178	0.146290	0.025322	0.000653	Cycle 146*	New Rate Constants & Err_K:	0.223179	0.143130	0.024130	0.000006
Cycle 55*	New Rate Constants & Err_K:	0.215576	0.146129	0.025260	0.000621	Cycle 147*	New Rate Constants & Err_K:	0.223183	0.143128	0.024129	0.000006
Cycle 56*	New Rate Constants & Err_K:	0.215954	0.145975	0.025200	0.000590	Cycle 148*	New Rate Constants & Err_K:	0.223187	0.143127	0.024129	0.000005
Cycle 57*	New Rate Constants & Err_K:	0.216313	0.145828	0.025147	0.000561	Cycle 149*	New Rate Constants & Err_K:	0.223190	0.143126	0.024128	0.000005
Cycle 58*	New Rate Constants & Err_K:	0.216655	0.145689	0.025095	0.000533	Cycle 150*	New Rate Constants & Err_K:	0.223193	0.143126	0.024128	0.000005
Cycle 59*	New Rate Constants & Err_K:	0.216980	0.145557	0.025045	0.000507	Cycle 151*	New Rate Constants & Err_K:	0.223197	0.143125	0.024127	0.000004
Cycle 60*	New Rate Constants & Err_K:	0.217288	0.145431	0.024999	0.000482	Cycle 152*	New Rate Constants & Err_K:	0.223200	0.143124	0.024127	0.000004
Cycle 61*	New Rate Constants & Err_K:	0.217582	0.145311	0.024954	0.000458	Cycle 153*	New Rate Constants & Err_K:	0.223202	0.143123	0.024126	0.000004
Cycle 62*	New Rate Constants & Err_K:	0.217861	0.145197	0.024912	0.000435	Cycle 154*	New Rate Constants & Err_K:	0.223205	0.143122	0.024126	0.000004
Cycle 63*	New Rate Constants & Err_K:	0.218127	0.145089	0.024872	0.000413	Cycle 155*	New Rate Constants & Err_K:	0.223208	0.143122	0.024126	0.000004
Cycle 64*	New Rate Constants & Err_K:	0.218379	0.144987	0.024834	0.000393	Cycle 156*	New Rate Constants & Err_K:	0.223210	0.143121	0.024125	0.000003
Cycle 65*	New Rate Constants & Err_K:	0.218619	0.144889	0.024798	0.000373	Cycle 157*	New Rate Constants & Err_K:	0.223213	0.143120	0.024125	0.000003
Cycle 66*	New Rate Constants & Err_K:	0.218847	0.144797	0.024764	0.000355	Cycle 158*	New Rate Constants & Err_K:	0.223215	0.143120	0.024125	0.000003

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Cycle 67*New Rate Constants & Err_K: 0.219064 0.144709 0.024732 0.000337
Cycle 68*New Rate Constants & Err_K: 0.219270 0.144625 0.024701 0.000320
Cycle 69*New Rate Constants & Err_K: 0.219467 0.144546 0.024672 0.000304
Cycle 70*New Rate Constants & Err_K: 0.219653 0.144471 0.024645 0.000289
Cycle 71*New Rate Constants & Err_K: 0.219830 0.144400 0.024619 0.000275
Cycle 72*New Rate Constants & Err_K: 0.219999 0.144332 0.024594 0.000261
Cycle 73*New Rate Constants & Err_K: 0.220159 0.144268 0.024570 0.000248
Cycle 74*New Rate Constants & Err_K: 0.220311 0.144207 0.024548 0.000236
Cycle 75*New Rate Constants & Err_K: 0.220456 0.144149 0.024526 0.000224
Cycle 76*New Rate Constants & Err_K: 0.220594 0.144094 0.024506 0.000213
Cycle 77*New Rate Constants & Err_K: 0.220725 0.144042 0.024487 0.000202
Cycle 78*New Rate Constants & Err_K: 0.220850 0.143993 0.024469 0.000192
Cycle 79*New Rate Constants & Err_K: 0.220968 0.143946 0.024451 0.000182
Cycle 80*New Rate Constants & Err_K: 0.221081 0.143902 0.024435 0.000173
Cycle 81*New Rate Constants & Err_K: 0.221188 0.143860 0.024419 0.000165
Cycle 82*New Rate Constants & Err_K: 0.221289 0.143820 0.024404 0.000156
Cycle 83*New Rate Constants & Err_K: 0.221386 0.143782 0.024390 0.000149
Cycle 84*New Rate Constants & Err_K: 0.221478 0.143746 0.024377 0.000141
Cycle 85*New Rate Constants & Err_K: 0.221566 0.143712 0.024364 0.000134
Cycle 86*New Rate Constants & Err_K: 0.221649 0.143680 0.024352 0.000127
Cycle 87*New Rate Constants & Err_K: 0.221728 0.143650 0.024341 0.000121
Cycle 88*New Rate Constants & Err_K: 0.221803 0.143621 0.024330 0.000115
Cycle 89*New Rate Constants & Err_K: 0.221874 0.143593 0.024319 0.000109
Cycle 90*New Rate Constants & Err_K: 0.221942 0.143568 0.024309 0.000104
Cycle 91*New Rate Constants & Err_K: 0.222007 0.143543 0.024300 0.000099
Cycle 92*New Rate Constants & Err_K: 0.222069 0.143520 0.024291 0.000094

Cycle 159*New Rate Constants & Err_K: 0.223217 0.143119 0.024124 0.000003
Cycle 160*New Rate Constants & Err_K: 0.223219 0.143119 0.024124 0.000003
Cycle 161*New Rate Constants & Err_K: 0.223221 0.143118 0.024124 0.000003
Cycle 162*New Rate Constants & Err_K: 0.223223 0.143118 0.024124 0.000003
Cycle 163*New Rate Constants & Err_K: 0.223224 0.143117 0.024123 0.000002
Cycle 164*New Rate Constants & Err_K: 0.223226 0.143117 0.024123 0.000002
Cycle 165*New Rate Constants & Err_K: 0.223228 0.143117 0.024123 0.000002
Cycle 166*New Rate Constants & Err_K: 0.223229 0.143116 0.024123 0.000002
Cycle 167*New Rate Constants & Err_K: 0.223230 0.143116 0.024122 0.000002
Cycle 168*New Rate Constants & Err_K: 0.223232 0.143116 0.024122 0.000002
Cycle 169*New Rate Constants & Err_K: 0.223233 0.143115 0.024122 0.000002
Cycle 170*New Rate Constants & Err_K: 0.223234 0.143115 0.024122 0.000002
Cycle 171*New Rate Constants & Err_K: 0.223235 0.143115 0.024122 0.000002
Cycle 172*New Rate Constants & Err_K: 0.223236 0.143114 0.024121 0.000002
Cycle 173*New Rate Constants & Err_K: 0.223238 0.143114 0.024121 0.000001
Cycle 174*New Rate Constants & Err_K: 0.223239 0.143114 0.024121 0.000001
Cycle 175*New Rate Constants & Err_K: 0.223239 0.143114 0.024121 0.000001
Cycle 176*New Rate Constants & Err_K: 0.223240 0.143114 0.024121 0.000001
Cycle 177*New Rate Constants & Err_K: 0.223241 0.143113 0.024121 0.000001
Cycle 178*New Rate Constants & Err_K: 0.223242 0.143113 0.024121 0.000001
Cycle 179*New Rate Constants & Err_K: 0.223243 0.143113 0.024121 0.000001
Cycle 180*New Rate Constants & Err_K: 0.223244 0.143113 0.024120 0.000001

*** CONVERGED ***

** Final Rate Constants: ** 0.223244 0.143113 0.024120