© *1992 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **65**, *553—558 (1992)*

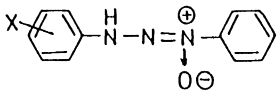
Molecular Interactions between Triazene 1-Oxides and Tetracyanoethylene

Ahmed Moukhtar Nour El-Din,* Alaa A. Hassan, Shaaban K. Mohamed,
Fathy F. Abd Elatif, and Hassan A. El-Faham
Chemistry Department, Faculty of Science, Minia University, El-Minia, A.R. Egypt
(Received February 28, 1991)

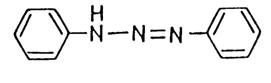
1,3-Diaryltriazene 1-oxides formed stable (1 : 1) charge-transfer complexes with tetracyanoethylene in different solvents, which were studied spectrophotometrically. The stability constants of the complexes were affected by substituents and solvent polarities. Likewise the thermodynamic properties ΔG, ΔH, and ΔS depend on the solvent polarities.

In continuation of our earlier studies on the physical and chemical interactions between 1,3-dipole systems, as nitrones,[1] 2*H*-pyrrole *N*-oxides,[2] isoindole *N*-oxides,[3] as well as azoxy compounds,[4] and electron-poor multiple bonded compounds, we have investigated the physical and chemical behavior of the 1,3-dipoles, unsymmetrical diaryltriazene 1-oxides,[5] towards different electron-poor and electron-rich compounds, specially the multiple bonded systems as tetracyanoethylene (TCNE) and *p*-benzoquinones.

In this work we present the results obtained from the interactions between the unsymmetrical diaryltriazene 1-oxides (**1a**—**k**) and TCNE in dichloromethane, ethyl acetate, and methanol.

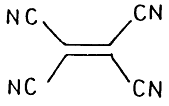


1



2

X, **a** = *o*-OCH_3
X, **b** = *m*-OCH_3
X, **c** = *p*-OCH_3
X, **d** = *o*-CH_3
X, **e** = *m*-CH_3
X, **f** = *p*-CH_3
X, **g** = -H
X, **h** = *o*-Cl
X, **i** = *m*-Cl
X, **j** = *p*-Cl
X, **k** = *p*-NO_2



TCNE

Experimental

TCNE was crystallized from chlorobenzene and sublimed, mp 198—199 °C. The unsymmetrical diaryltriazene 1-oxides (**1a**—**k**) were prepared according to the literature.[6] The analytical and physical data are summarized in Tables 1 and 2. The organic solvents used in the present investigation, dichlo-

Table 1. Physical and Analytical Data of Aryltriazene 1-Oxide **1a**—**k**

Compound	Mp/°C (lit)	Color	Solvent of recrystallization	Yield %	Mol. formula (M. wt)	Analysis/% Found (Calcd) C	H	N	Ref.
1a	92—94	Pale yellow	Ethanol	71	$C_{13}H_{13}N_3O_2$	64.20	5.43	17.19	
					(243.264)	(64.18	5.40	17.30)	
1b	101—102	Orange	Ethanol	69	$C_{13}H_{13}N_3O_2$	64.19	5.42	17.34	
					(243.264)	(64.18	5.40	17.30)	
1c	113—114								6
	(114)								
1d	95—97	Yellow	Petroleum ether	75	$C_{13}H_{13}N_3O$	68.93	5.78	18.34	
					(227.264)	(68.70	5.77	18.49)	
1e	127—128	Yellow	Ethanol	78	$C_{13}H_{13}N_3O$	68.80	5.73	18.48	
					(227.264)	(68.70	5.77	18.49)	
1f	130—131								6
	(131)								
1g	126—127								6
	(127)								
1h	72—73	Yellowish brown	Petroleum ether	86	$C_{12}H_{10}N_3OCl$	58.13	4.13	16.99	
					(247.683)	(58.19	4.07	16.97)	
1i	143—144	Yellow	Ethanol	72	$C_{12}H_{10}N_3OCl$	58.07	4.05	16.82	
					(247.683)	(58.19	4.07	16.97)	
1j	146—147								6
	(146)								
1k	183—184								6
	(182)								

Table 2. The ^{1}H NMR , IR, and MS Spectral Data of Compounds **1a**—**k**

Compd	^{1}H NMR (δ, $CDCl_3$)	IR (KBr, cm^{-1})	MS m/z (rel intensity/%)
1a	3.90 (s, 3H) OCH_3; 6.85—8.15 (m, 9H) Ar-H; 10.95 (s, br, 1H) NH.	3285 (NH); 1510 (>N-N=N-); 1330 (N→O).	243 (M$^+$, 5); 199 (2); 168 (2); 135 (39); 107 (16); 92 (34); 77 (100); 65 (26); 51 (31).
1b	3.85 (s, 3H) OCH_3; 6.55—8.15 (m, 9H) Ar-H; 10.80 (s, br, 1H) NH.	3190 (NH); 1450—1500 (>N-N=N-); 1330 (N→O).	243 (M$^+$, 6); 215 (1); 199 (6); 168 (2); 135 (25); 107 (100); 92 (27); 77 (89); 65 (13); 51 (24).
1c	3.80 (s, 1H) OCH_3; 6.80—8.20 (m, 9H) Ar-H; 10.85 (s, br, 1H) NH.	3150 (NH); 1515 (>N-N=N-); 1325 (N→O).	243 (M$^+$, 6); 215 (5); 199 (9); 168 (3); 135 (37); 107 (83); 92 (25); 77 (100); 65 (21); 51 (35).
1d	2.33 (s, 3H) CH_3; 6.80—8.30 (m, 9H) Ar-H; 10.93 (s, br, 1H) NH.	3230 (NH); 1510 (>N-N=N-); 1330 (N→O).	227 (M$^+$, 4); 183 (21); 168 (5); 119 (24); 107 (17); 91 (100); 65 (31); 51 (29).
1e	2.30 (s, 3H) CH_3; 6.80—8.15 (m, 9H) Ar-H; 10.90 (s, br, 1H) NH.	3180—3200 (NH); 1460—1480 (>N-N=N-); 1335 (N→O).	227(M$^+$, 7); 183 (10); 168 (3); 119 (30); 107 (17); 91 (100); 77 (38); 65 (23); 51 (18).
1f	2.35 (s, 3H) CH_3; 6.90—8.18 (m, 9H) Ar-H; 10.90 (s, br, 1H) NH.	3190 (NH); 1520 (>N-N=N-); 1310—1325 (N→O).	227 (M$^+$, 7); 183 (9); 168 (2); 119 (31); 107 (17); 91 (100); 77 (36); 65 (21); 51 (17).
1g	7.00—8.15 (m, 10H) Ar-H; 10.80 (s, br, 1H) NH.	3200 (NH); 1510 (>N-N=N-); 1315 (N→O).	213 (M$^+$, 6); 169 (10); 108 (3); 105 (38); 77 (100); 51 (24).
1h	6.90—8.20 (m, 9H) Ar-H; 11.10 (s, br, 1H) NH.	3260—3280 (NH); 1510 (>N-N=N-); 1295—1340 (N→O).	247.5 (M$^+$, 5); 203.5 (2); 167.5 (3); 139.5 (43); 111.5 (100); 77 (34); 51 (23).
1i	6.95—8.20 (m, 9H) Ar-H; 11.30 (s, br, 1H) NH.	3220 (NH); 1440—1510 (>N-N=N-); 1340 (N→O).	247.5 (M$^+$, 5); 203.5 (1); 167.5 (2); 139.5 (52); 111.5 (100); 77 (36); 51 (23).
1j	6.95—8.15 (m, 9H) Ar-H; 10.80 (s, br, 1H) NH.	3190 (NH); 1510 (>N-N=N-); 1330 (N→O).	247.5 (M$^+$, 6); 203.5 (2); 167.5 (3); 139.5 (52); 111.5 (100); 77 (39); 51 (25).
1k	7.20—8.35 (m, 9H) Ar-H; 11.00 (s, br, 1H) NH.	3200 (NH); 1510 (>N-N=N-); 1330 (N→O).	258 (M$^+$, 5); 214 (3); 150 (6); 122 (100); 108 (10); 92 (28); 77 (46); 65 (7); 51 (19).

romethane, 1,2-dichloroethane, chloroform, chlorobenzene, methanol, and benzene were purified following Vogel[7] and Organikum,[8] dried and distilled. Donors (**1a**—**k**) and acceptor TCNE concentrations ranged from 1×10^{-2} to 1×10^{-1} M (1 M=1 mol dm^{-3}). Dichloromethane was used as a solvent for the study of all CT complexes. Stock solutions (3×10^{-2} M) of donors and acceptor were prepared for determination of the stoichiometry by Job's method.[9] The effect of temperature on the formation and stability of CT complexes in CH_2Cl_2 was determined by increasing the temperature of the all gradually from 10 to 35 °C (±0.5 °C) and decreasing it from 35 to 10 °C with the same sample. Whenever the change of the intensity was not reversible, the donor-acceptor pair in question was not regarded as forming a stable CTC. The association constants at different temperatures were determined by using the Benesi-Hildebrand's method[10] by increasing the temperature gradually from 10 to 35 °C for each concentration, the electronic spectra were recorded within a wavelength range 350—850 nm, using Perkin-Elmer Lambda 2 (with thermostated cell holder) spectrophotometer in a matched pair of stoppered fused silica cells of 1.0 cm optical path length. All melting points are uncorrected, IR spectra were recorded on a Shimadzu 408 spectrophotometer, ^{1}H NMR spectra on a Bruker WP 80 WG (80 MHz) spectrophotometer. Elemental analyses of new compounds were carried out by Fach. Chemie, Universität Duisburg (FRG).

Results and Discussion

According to the structural features of the triazene 1-oxide system, it might be considered as containing two active centers; the first one is the azoxy 1,3-dipole $(-\underset{\overset{\downarrow}{O}}{N}=N-)$, and the second one is the nucleophilic 3-nitrogen atom. Therefore, it may be expected that triazene 1-oxides should undergo 1,3-dipolar cycloaddition reactions with dipolarophiles.[11] On the other hand, they might behave as nucleophiles towards various electrophilic compounds through their 3-nitrogen atom.

On mixing of equimolar solutions of the 1,3-dipoles triazene 1-oxides (**1a**—**j**) and electron-deficient dipolarophile TCNE in dichloromethane at room temperature, deeply blue stable CT complexes have been obtained. They exhibit the characteristic[12] broad absorption bands in the visible region 575—705 nm (Table 3). The chromatographic isolation of the mixtures after 4 days yielded both reactants, TCNE and triazene 1-oxides. On the other hand, the isolation of each of the CT complexes after the recording of their spectrum at 35 °C, on thin-layer plates, shows that, each mixture contains only both donor and TCNE compounds except the mixture of **1c** and TCNE (Table 4). This behavior can be attributed to the strong mesomeric effect of the electron-donating group OCH_3 which decreases the stability of the triazene 1-oxide (**1c**). This feature is in agreement with the results obtained by T. Mitsuhashi et al.[5] Moreover, heating the reaction mixtures in ethyl acetate and methanol did not lead to any reaction

Table 3. Thermodynamic and Spectrophotometric Results of Triazene 1-Oxides **1a**—**j** with TCNE Complexes

Donor	λ_{max}	K_{CT}/l mol^{-1}						ε	$-\Delta G$	$-\Delta H$	$-\Delta S$	i. p.	E
	nm	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	l mol^{-1} cm^{-1}	kcal mol^{-1}	kcal mol^{-1}	cal mol^{-1} K^{-1}	eV	eV
1a	690	7.547 $\pm3.3\times10^{-4}$	6.666 $\pm6\times10^{-4}$	6.638 $\pm6\times10^{-4}$	5.8146 $\pm5\times10^{-4}$	5.579 $\pm1.58\times10^{-4}$	5.330 $\pm6.12\times10^{-4}$	100	1.096 $\pm8.06\times10^{-2}$	2.760 $\pm8.2\times10^{-3}$	5.676 $\pm2.8\times10^{-3}$	7.601	1.797
1b	643	5.854 $\pm2.9\times10^{-4}$		4.897 $\pm3.94\times10^{-4}$	4.572 $\pm2.58\times10^{-4}$	4.318 $\pm2.58\times10^{-4}$		76	0.921 $\pm5.26\times10^{-2}$	2.338 $\pm7.9\times10^{-3}$	4.839 $\pm1.77\times10^{-3}$	7.776	1.928
1c	705			6.769 $\pm2\times10^{-4}$				142				7.550	1.759
1d	650	6.796 $\pm2.23\times10^{-4}$	6.454 $\pm1.2\times10^{-4}$	6.238 $\pm2.08\times10^{-4}$	5.415 $\pm3.8\times10^{-4}$			125	1.061 $\pm2.30\times10^{-3}$	2.550 ±0.01	5.088 ±0.032	7.748	1.908
1e	641	5.168 $\pm3.6\times10^{-4}$		4.832 $\pm4.47\times10^{-4}$	4.473 3.65×10^{-4}	4.194 $\pm2.9\times10^{-4}$		100	0.870 $\pm5.9\times10^{-3}$	2.226 $\pm7.1\times10^{-3}$	4.683 $\pm3.27\times10^{-3}$	7.784	1.934
1f	668	7.184 $\pm1.25\times10^{-4}$	6.571 $\pm2.23\times10^{-4}$	6.468 $\pm2.1\times10^{-4}$	5.637 $\pm2.1\times10^{-4}$	5.418 $\pm4.47\times10^{-4}$		71.	1.082 $\pm2.4\times10^{-3}$	2.602 $\pm1\times10^{-4}$	5.189 $\pm2.27\times10^{-4}$	7.680	1.856
1g	620	6.414 $\pm4.77\times10^{-4}$		4.032 $\pm2.11\times10^{-4}$	3.891 $\pm3.16\times10^{-4}$	3.646 $\pm3.16\times10^{-4}$	3.553 $\pm3.16\times10^{-4}$	111	0.786 $\pm2.01\times10^{-3}$	1.821 $\pm4.3\times10^{-3}$	3.459 $\pm5\times10^{-4}$	7.871	2.000
1h	575	2.531 $\pm1.21\times10^{-4}$		2.347 $\pm6.2\times10^{-4}$	2.178 $\pm1.5\times10^{-4}$		1.9194 $\pm4.47\times10^{-4}$	83	0.494 ±0.056	1.386 $\pm1.06\times10^{-2}$	3.043 $\pm1.95\times10^{-3}$	8.080	2.157
1i	585	3.048 $\pm2.98\times10^{-4}$	2.744 $\pm3.33\times10^{-4}$	2.583 $\pm2.98\times10^{-4}$	2.499 $\pm1\times10^{-6}$	2.431 $\pm2.98\times10^{-4}$	2.340 $\pm1.41\times10^{-4}$	83	0.550 $\pm3.9\times10^{-2}$	1.469 $\pm6\times10^{-3}$	3.136 $\pm1.36\times10^{-3}$	8.031	2.119
1j	605	3.804 $\pm4.47\times10^{-4}$		3.544 $\pm3.87\times10^{-4}$	3.501 $\pm5\times10^{-4}$	3.287 $\pm5.9\times10^{-4}$	3.039 $\pm2.98\times10^{-4}$	90	0.733 $\pm5.16\times10^{-2}$	1.718 $\pm6.3\times10^{-3}$	3.362 $\pm1.7\times10^{-3}$	7.937	2.049

Table 4. Thermodynamic Parameters of CT Complexes of Triazene 1-Oxide **1e** with TCNE in Different Solvents

Solvent	λ_{max}	K_{CT}/l mol^{-1}						ε	$-\Delta G$	$-\Delta H$	$-\Delta S$	Dielectric[22] constant 25 °C
	nm	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	l mol^{-1} cm^{-1}	kcal mol^{-1}	kcal mol^{-1}	cal mol^{-1} K^{-1}	
Chlorofom	655	6.300 $\pm2.5\times10^{-4}$	5.775 $\pm2.98\times10^{-4}$	4.970 $\pm2.1\times10^{-4}$	4.760 $\pm3.33\times10^{-4}$	4.660 $\pm4.47\times10^{-4}$		142	0.929	2.644	5.853	4.8
Dichloromethane	641	5.168 $\pm3.6\times10^{-4}$		4.832 $\pm4.47\times10^{-4}$	4.473 $\pm3.65\times10^{-4}$	4.194 $\pm2.9\times10^{-4}$		100	0.870	2.226	4.683	8.9
1,2-Dichloroethane	643	5.250 $\pm5\times10^{-4}$	4.680 $\pm2.2\times10^{-4}$	4.591 $\pm2.2\times10^{-4}$	4.411 $\pm3.87\times10^{-4}$			125	0.881	2.335	4.956	10.65
Chlorobenzene	647	5.400 $\pm3.87\times10^{-4}$	4.800 $\pm3.87\times10^{-4}$	4.680 $\pm5\times10^{-4}$	4.551 $\pm3.87\times10^{-4}$	4.320 $\pm3.33\times10^{-4}$	4.141 $\pm3.33\times10^{-4}$	111	0.894	2.461	5.349	5.62
Benzene	636	4.680 $\pm3.87\times10^{-4}$		4.500 $\pm3.87\times10^{-4}$	4.307 $\pm3.16\times10^{-4}$	4.105 $\pm3.33\times10^{-4}$	4.00 $\pm5.16\times10^{-4}$	83	0.845	1.626	2.576	2.284

between them, instead, the triazene 1-oxides were decomposed. This result indicates that, the 1,3-dipole system in the triazene 1-oxide compounds, i.e. $-\underset{\overset{\downarrow}{O}}{N}=N-$, shows no tendency towards the dipolarophile TCNE. This behavior is in agreement with the results obtained from the study of the reactions of the azoxy compounds with different dipolarophiles by Huisgen.[13] That the triazene 1-oxides (**1a**—**k**) did not undergo a nucleophilic reaction with TCNE, may be due to the mesomeric effect of pair electron of the 3-nitrogen atom with the 1,3-dipole azoxy group $(-\underset{\ominus|\underline{O}|}{\overset{\oplus}{N}}=\bar{N}-\bar{N}\langle \leftrightarrow -\underset{\ominus|\underline{O}|}{\bar{N}}-\bar{N}=\overset{\oplus}{N}\langle)$.

On the other hand, G.M. Camaggi et al.[14] has been reported that, the treatment of 1,3-di-*p*-tolyltriazene with TCNE in methanol afforded *N*-dicyanomethylene-*p*-toluidine, 2-*p*-tolylhydrazonopropanedinitrile and other products via the formation of unstable deeply blue CTC's as a first step. Also, a new mechanism for the formation of these products was suggested by Mitsuhashi.[15,16] These results confirm the important role of the oxygen atom, which not only leads to decrease the nucleophilic reactivity of the 3-nitrogen atom of the triazene 1-oxide system towards TCNE, but also is responsible for the formation of stable CTC's with TCNE, as a consequence for the presence of a negative charge on the oxygen atom, which should make the triazene 1-oxide a better electron donor according to the charge-transfer theory.[17] The fact that, azobenzene did not form CTC with TCNE,[4] while azoxybenzene formed stable CTC with the same acceptor, supported our results. It should also be noted that, the CT complexes of azoxybenzene and 4,4′-azoxyanisole with TCNE absorbed at shorter wavelength (500 sh and 570 nm, respectively)[4] than the analogous triazene 1-oxides (Table 3). This may indicates that the presence of an NH group in the triazene 1-oxide system increases their basicity and consequently increases the ability to complexation with TCNE.

Application of Job's method shows that the stoichiometric ratio for the formed CTC's is 1 : 1. The association constants K_{ct} of the CTC's examined were determined at six different temperatures (Table 3). The values of K_{ct} were used to calculate the enthalpies of complex formation (ΔH) (Table 3) using the van't Hoff equation plots. The values of change in free energy (ΔG) and entropy (ΔS) for CTC's which are given in this table have been derived from the reported values of ΔH and from the association constants (K_{ct}). The data reported in Table 3 show also that the CT-maxima values follow, in general, the order expected from the electron donating character of the diaryltriazene 1-oxides (**1a**—**j**), namely $OCH_3>CH_3>H>Cl$. It is interesting in this respect to note that, in case of CTC's of the methylated and methoxylated diaryltriazene 1-oxides (**1a**—**f**) with TCNE, the base strength of these donors follow the order: para>ortho>meta; while for the chlorinated diaryltriazene 1-oxides (**1h**—**j**) it follows the order: para>meta>ortho. This trend is in agreement with the normal principles of the inductive and mesomeric effects of the nature of substituents.[18—20] From the data reported in Table 3 the donor (**1k**) did not form CTC with TCNE. Presumably, this is a nature consequence of the low donating ability of this donor, which arises from the electron withdrawing effect of the nitro group present on the phenyl ring of the donor. Thus, a plot of log K_{ct} against Hamett's σ values[21] is linear with slope of $\rho=-0.666$, $r^*=-0.989$ (Fig. 1), this is in accord with the expectation, since a negative value of σ is typical of a reaction enhanced by electron donors acting on the reactive center.

According to Mulliken's theory,[17] the strength of the interaction between a donor and an acceptor increases with increasing the molar extinction coefficient. However, in the present work, ε_{max} values, unlike K_{ct} values, show large deviation. The CTC's which have low stability constants are found to have higher ε_{max} values. This behavior can be attributed to the steric effect of the different substituents.[12]

The ionization potential values of the donors listed in Table 3, were estimated from the energies of the CT-bands applying the well-known empirical equation:[21] $\text{i.p.}=a\pm b\bar{\nu}_{CT}$. As seen in Table 3, the i.p. values of donors (**1a**—**j**) vary regulary with the transition energies of the corresponding CTC's. This is in agreement with the previously reported results.[12,21] From the data in Table 3, as ΔH values decrease, corresponding decrease in ΔS is also observed. This simultaneous decrease in these thermodynamic parameters may serve as an indi-

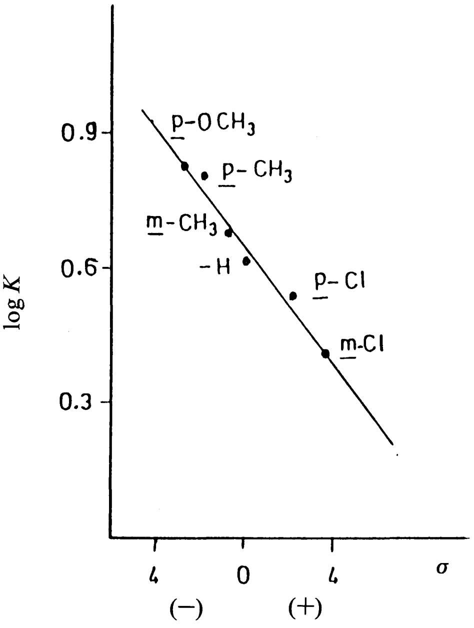


Fig. 1. Hammett plot for complex formation between TCNE with some *m*- and *p*-substituted triazene 1-oxides.

cation of the physical restraints imposed upon the complex components as the strength of the interaction between them increases. A linear relationship between ΔH and ΔS (Fig. 2) usually shown by series of related equilibria involving moderate changes in structure,[22] is also indication for this behavior; where the slope 509 K represents the so-called "isokinetic temperature".[23] The experimental results in Table 3 also show that the values of the thermodynamic and spectrophotometric properties are markedly affected by variation of the substituents in the diaryltriazene 1-oxides studied.

It is well known that[12] in the case of weak complexes the role of the solvent is very important. In our case, the different values of equilibrium constants of the triazene 1-oxide (**1e**)–TCNE complex in different solvents (Table 4) suggest that, the role of solvent interaction with TCNE can not be neglected. Comparison of the results in Table 4 reveals that, in case of $CHCl_3$, in spite of lower dielectric constant (4.8),[24] it shows a higher absorption data than the other solvents, this may be due to the ability of chloroform to form a hydrogen bond with the negatively charged oxygen atom of triazene 1-oxide. The anomalous solvent effect on K_{ct} values in CH_2Cl_2 and $ClCH_2$–CH_2Cl may be attributed to the complexation of these solvents with the acceptor TCNE, which should lead to a decrease of K_{ct} values. A similar behavior has been previously reported on substituted indoles and TCNE by Cipiciani and Santini.[25]

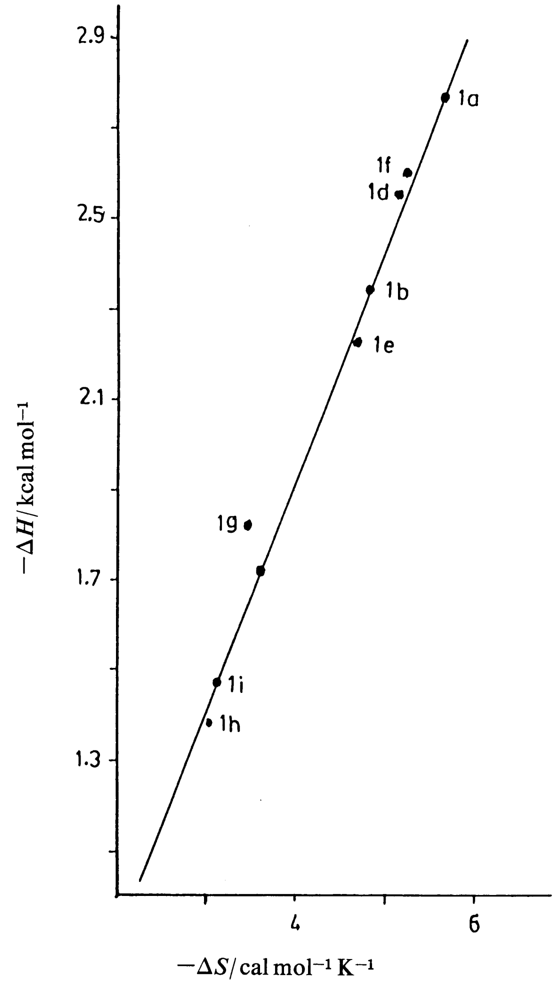


Fig. 2. Relationships between enthalpies and entropies of formation for CT complexes of a series of triazene 1-oxide derivatives with TCNE.

On the other hand, the stability of the **1e**–TCNE complex in the aromatic hydrocarbon solvents; i.e. benzene and chlorobenzene, increases with increasing the polarity of solvents. This behavior is expected because an increase of the solvent polarity should favor the stabilization of the excited state of the complex relative to its ground state, thereby reducing the energy requirements for transitions.[26]

We warmly thank Professor Dr. D. Döpp, Fachbereich Chemie, Duisburg Universität (FRG) for the providing laboratory facilities and for helpful discussions.

References

1) A. M. Nour El-Din, *Spectrochim. Acta, Part A*, **41**, 721 (1985).

2) A. M. Nour El-Din, *Bull. Chem. Soc. Jpn.*, **59**, 1239 (1986).

3) A. M. Nour El-Din and D. Döpp, *Bull. Soc. Chim. Belg.*, **93**, 891 (1984).

4) A. M. Nour El-Din, *Gazz. Chim. Ital.*, **115**, 401 (1985).

5) T. Mitsuhashi, Y. Osamura, and O. Simamura, *Tetrahedron Lett.*, **30**, 2593 (1965).

6) T. Mitsuhashi and O. Simamura, *J. Chem. Soc. B*, **1970**, 705.

7) Vogel's, "Text Book of Practical Organic Chemistry," 4th ed, Longman, London (1978).

8) Organikum, "Practical Handbook of Organic Chemistry," 1st ed, Pergamon Press, Oxford (1973).

9) P. Job, *Justus Liebigs Ann. Chem.*, **10**, 113 (1928).

10) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

11) R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976), and references cited therein.

12) R. Foster, "Organic Charge Transfer Complexes," Academic Press, London (1969).

13) R. Huisgen and F. P. Gambra, *Tetrahedron Lett.*, **23**, 55 (1982).

14) C. M. Camaggi, R. Leardini, and C. Chatgilialoglu, *J. Org. Chem.*, **42**, 2611 (1977).

15) T. Mitsuhashi, C. Matsumura, and Y. Koga., *J. Chem. Soc., Chem. Commun.*, **1986**, 257.

16) T. Mitsuhashi, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 1495.

17) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

18) A. M. Nour El-Din, *Bull. Soc. Chim. Belg.*, **95**, 1041 (1986).

19) A. E. Mourad, A. M. Nour El-Din, A. A. Hassan, and D. Döpp., *Bull. Soc. Chim. Belg.*, **95**, 1045 (1986).

20) A. M. Nour El-Din, A. E. Mourad, A. A. Hassan, and D. Döpp., *Z. Phys. Chem. (Leipzig)*, **269**, 832 (1988).

21) R. E. Merrifield and W. D. Philips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

22) G. Reichenbach, S. Santini, and U. Massucato, *J. Chem. Soc., Faraday Trans. 1,* **61**, 142 (1973).
23) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York (1963).
14) "Handbook of Chemistry and Physics," 60 th ed, ed by R-C. Weast, CRC-Press, West Palm Beach, Fla. (1979—1980).
25) A. Cipiciani, S. Santini, and G. Savelli, *J. Chem. Soc., Faraday Trans. 1,* **75**, 497 (1979).
26) B. B. Bhowmik and S. Chattopadhyay, *Spectrochim. Acta, Part A,* **37**, 445 (1981).