J. Am. Chem. Soc. 1982, 104, 5127-5133

erically pure *cis*- and *trans*-1-methyl-4-*tert*-butyl-1-silacyclohexane (see Scheme I). Their experiments were carried out at 0 °C, and their product yields in CCl_4 and in $CHCl_3$ can be used to calculate the inversion rate constants k_1 and k_{-1} at this temperature with the assumption that the cis- and trans-silyl radicals react with the chlorinating agent at the same rate. That is, $k_{cis} = k_{trans} = 3.78 \times 10^9\ M^{-1}$ and $2.07 \times 10^8\ M^{-1}\ s^{-1}$ for CCl_4 (see Table I) and $CHCl_3$ (see Table II), respectively, at 0 °C. The data tabulated by Sakurai and Murakami[53] yield $k_1 = 6.4 \times 10^9\ s^{-1}$ (CCl_4) and $11.5 \times 10^9\ s^{-1}$ ($CHCl_3$) and $k_{-1} = 2.9 \times 10^9\ s^{-1}$ (CCl_4) and $4.3 \times 10^9\ s^{-1}$ ($CHCl_3$). The two chlorinating solvents yield individual inversion rate constants k_1 and k_{-1} which are in good agreement. More importantly, these rate constants are in the same range as that calculated for the inversion of Sommer and Ulland's[48] (1-naphthyl)phenylmethylsilyl radical.

Acknowledgment. Thanks are due to Mr. S. E. Sugamori for his technical assistance.

Registry No. $Et_3Si\cdot$, 24669-77-0; $(CH_3)_2CHI$, 75-30-9; CH_3CH_2I, 75-03-6; CH_3I, 74-88-4; C_6H_5I, 591-50-4; $CH_2{=}CHCH_2Br$, 106-95-6; $C_6H_5CH_2Br$, 100-39-0; $(CH_3)_3CBr$, 507-19-7; $CH_3(CH_2)_4Br$, 110-53-2; *c*-C_3H_5Br, 4333-56-6; C_6H_5Br, 108-86-1; CCl_4, 56-23-5; $CH_2{=}CHCH_2Cl$, 107-05-1; $C_6H_5CH_2Cl$, 100-44-7; $(CH_3)_3CCl$, 507-20-0; $CH_3(CH_2)_4Cl$, 543-59-9; C_6H_5Cl, 108-90-7; $C_6H_5CH_2F$, 350-50-5; $CHCl_3$, 67-66-3; CH_2Cl_2, 75-09-2; Cl_3CCCl_3, 67-72-1; Cl_2CHCCl_3, 76-01-7; $ClCH_2CCl_3$, 630-20-6; CH_3CCl_3, 71-55-6; $Cl_2CHCHCl_2$, 79-34-5; $N{\equiv}CCCl_3$, 545-06-2.

Supplementary Material Available: Tables of absolute rate constants for reactions of triethylsilyl radical with alkyl and aryl halides (31 pages). Ordering information is given on any current masthead page.

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Intramolecular Charge-Transfer Absorption and Emission Resulting from Through-Bond Interaction in Bichromophoric Molecules

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Contribution from the Laboratory for Organic Chemistry, University of Amsterdam, 1018 WS Amsterdam, The Netherlands. Received September 16, 1981

Abstract: A series of molecules is studied (**1–9** in Scheme I) that incorporate an electron-donor (D) and an electron-acceptor (A) chromophore connected by various alicyclic frameworks. The conformation of the latter prevents close approach of D and A. Nevertheless, intramolecular charge-transfer (CT) interaction between D and A is evident from the absorption and emission spectra for many of the molecules studied. It is concluded that the mode of interaction must be mainly of the through-bond type (TBI). The results indicate that under favorable circumstances such TBI leads to discrete intramolecular CT absorption and emission even if D and A are separated by as many as five σ bonds. It is proposed that TBI may be of significance in many bichromophoric molecules, the photophysical properties of which have heretofore only been discussed within the framework of through-space interactions (TSI). Finally the present results allow formulation of a tentative set of conditions that govern the appearance of a discrete optical transition due to TBI in bichromophoric molecules.

The photophysical properties of bichromophoric molecules containing two chromophores (M, M′) connected by a saturated paraffinic moiety (e.g., M–$(CH_2)_n$–M′) have been studied extensively.[1] In many cases the occurrence of intramolecular exciplex type emission[1,2] or intramolecular charge-transfer (CT) absorption[3,4] was reported. The mode of interaction between the chromophores responsible for these phenomena has largely, although not exclusively,[5,6] been considered to be through-space interaction (TSI) and thus to be limited to molecules that adopt a "folded" conformation, which allows direct overlap between the chromophores in the ground or excited state.

In other fields of spectroscopy (e.g., photoelectron spectroscopy[7]), however, ubiquitous data have been collected to show the possibility of interaction between two functional groups via limited[8] arrays of σ bonds (i.e., through-bond interaction TBI) as theoretically predicted by Hoffmann et al.[14] Although both TSI and TBI are expected[14,15] to be conformation dependent, the latter is certainly not limited to "folded" conformations and thus provides a mode of intramolecular interaction in bichromophoric molecules adopting various "stretched" conformations as well as one that may add considerably to the overall interaction[16] (i.e., TSI + TBI)

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(1) For a review, see: de Schrijver, F. C.; Boens, N.; Put, J. *Adv. Photochem.* **1977**, *10*, 359–465.

(2) Borkent, J. H.; de Jong, A. W. J.; Verhoeven, J. W.; de Boer, Th. J. *Chem. Phys. Lett.* **1978**, *57*, 530–534.

(3) Craenen, H. A. H.; Verhoeven, J. W.; de Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 405–416 and references cited therein.

(4) Smirnov, E. A. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1955**, *25*, 2429–2433.

(5) Hudec, J. *J. Chem. Soc., Chem. Commun.* **1970**, 829–831.

(6) de Gee, A. J.; Sep, W. J.; Verhoeven, J. W.; de Boer, Th. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 579–583, 670–675.

(7) Gleiter, R. *Angew. Chem.* **1974**, *86*, 770–775 and references cited therein.

(8) TBI over three σ bonds has been studied most extensively.[7,9] Significant interaction over four,[10,11,12] five,[12] and even six σ bonds[13] has, however, recently been detected by photoelectron spectroscopy.

(9) For a recent example of remarkably effective TBI over three bonds, see: Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 44–48.

(10) Martin, H. D.; Schwesinger, R. *Chem. Ber.* **1974**, *107*, 3143–3145.

(11) Paddon-Row, M. N.; Patney, H. K.; Brown, R. S.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5575–5577.

(12) Dougherty, D.; Brint, P.; McGlynn, S. P. *J. Am. Chem. Soc.* **1978**, *100*, 5597–5603.

(13) M. N. Paddon-Row, private communication.

(14) (a) Hoffman, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499–1509. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9.

(15) Schoeller, W. W. J. *Chem. Soc., Perkin Trans. 2* **1979**, 366–368.

(16) Simultaneous operation of TSI and TBI in the enforced folded conformation of [*n.n*]paracyclophanes (*n* = 2, 3) was convincingly shown by Heilbronner et al.[17,18]

(17) Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1974**, *57*, 151–159.

0002-7863/82/1504-5127$01.25/0

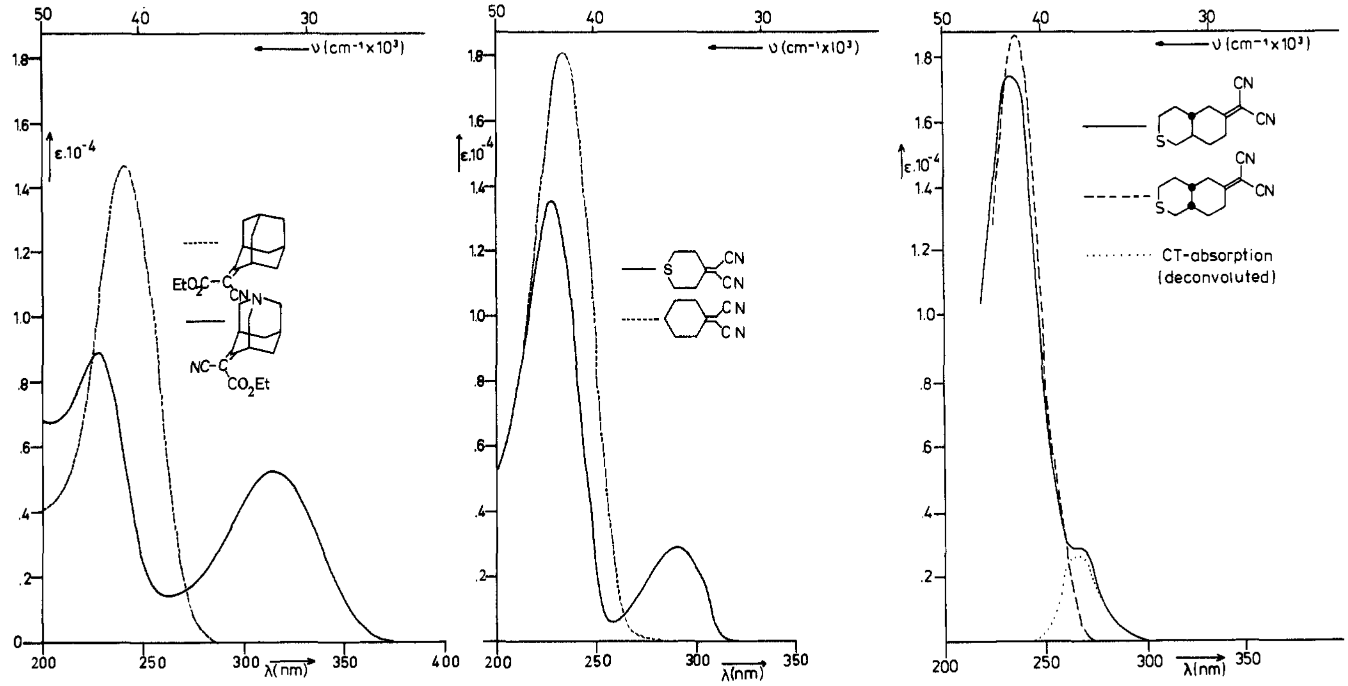

Figure 1. Absorption spectra (in *n*-hexane) of some bichromophoric molecules together with those of "isolated" acceptor models.

Scheme I. Bichromophoric Systems Studied (1-9) and Models (10, 11) for the "Isolated" Acceptor Chromophores

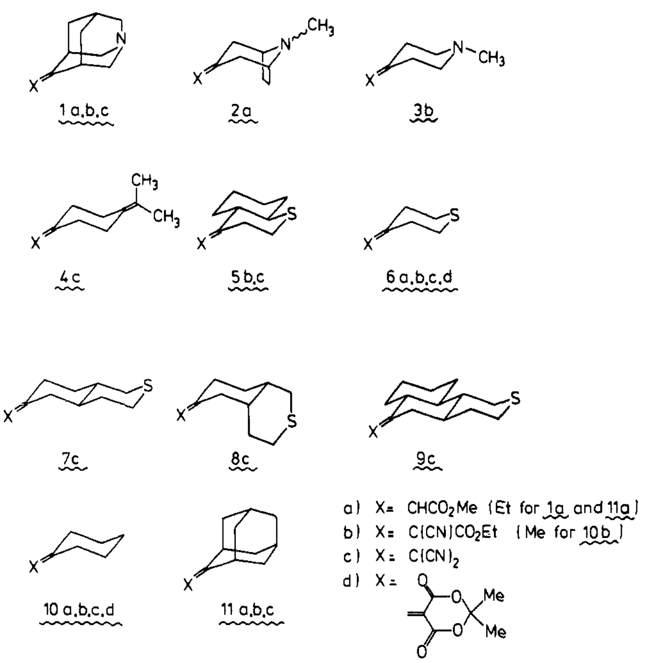

Table I. Absorption Data (See Also Ref 19) for Bichromophoric Systems 1-9 and Reference Chromophores 10 and 11[a]

compd	type of transition: A → A*	CT	$-\beta_{12}$(eV)
1a	48.3 [12 630]	36.4 [4530]	0.33
1b	43.7 [8 780]	31.6 [4900]	0.65
1c	43.9 [8 300]	31.5 [4500]	0.64
2a	47.6 [11 500]	40.0 [1775]	0.20
3b	41.7 [14 000]		0
4c	43.9 [13 000]	36.8 [3300]	0.37
5b	42.9 [11 960]	34.5 [2270]	0.43
5c	42.8 [13 720]	33.8 [2670]	0.49
6a	47.6 [15 700]	39.4 [2920]	0.26
6b	43.9 [10 000]	35.2 [2100]	0.36
6c	43.9 [13 500]	34.5 [2860]	0.41
6d	43.5 [9 870]	32.9 [1910]	0.44
7c	42.9 [17 600]	37.0 [2630][b]	0.27
8c	42.6 [18 500]		0
9c	42.2 [15 400]	37.7 [2000][b]	0.20
10a	45.9 [15 400]		
10b	42.7 [14 700]		
10c	42.8 [18 200]		
10d	42.2 [10 000]		
11a	44.6 [18 150]		
11b	41.3 [14 400]		
11c	41.3 [12 000]		

[a] All in *n*-hexane at 20 °C: $\nu_{\max}$ (cm⁻¹ × 10³) [$\epsilon_{\max}$ (L mol⁻¹ cm⁻¹)] and calculated β_{12} values (cf. text). [b] Deconvoluted values (cf. Figure 1).

in "folded" conformations. Several previous reports from our laboratory[6,19] as well as from other investigators[5,20] have already indicated the possibility of observing CT-type absorption bands for bichromophoric systems conformationally restricted as to avoid TSI.

We describe in this paper a systematic study on the question whether TBI in "stretched" conformations can lead not only to the observation of intramolecular CT absorption but also to that of intramolecular exciplex[21] emission. The answer to this question will turn out to be unequivocally albeit not unconditionally positive.

The question as to which degree TBI adds to the overall interaction responsible for exciplex emission from "folded" conformations will be left untouched for the moment, particularly because of the large problems[22] in defining criteria for quantitative separation of TBI and TSI in systems where both are operative.

With these objectives in mind a series of bichromophoric molecules was synthesized (cf. Scheme I) containing a potential electron-donor function (i.e., an amino group in **1**, **2**, and **3**, an

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(18) Kovac, B.; Mohraz, M.; Heilbronner, E.; Boekelheide, V.; Hopf, H. *J. Am. Chem. Soc.* **1980**, *102*, 4314–4324.

(19) (a) Dekkers, A. W. J. D.; Verhoeven, J. W.; Speckamp, W. N. *Tetrahedron* **1973**, *29*, 1691–1696. (b) Pasman, P.; Verhoeven, J. W.; de Boer, Th. J. *Tetrahedron* **1976**, *32*, 2827–2830. (c) Pasman, P.; Verhoeven, J. W.; de Boer, Th. J. *Tetrahedron Lett.* **1977**, 207–210.

(20) Tickle, I.; Hess, J.; Vos, A.; Engberts, J. B. F. N. *J. Chem. Soc., Perkin Trans. 2* **1978**, 460–465.

(21) The term exciplex is used in this context only to indicate excited-state electronic interaction.

(22) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936–967.

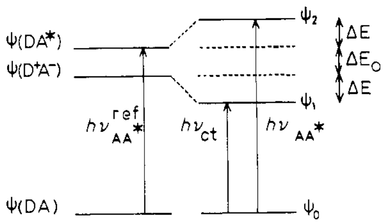

Figure 2. Configuration interaction between the pure CT excited configuration ($\psi(D^+A^-)$) and a locally in A excited configuration ($\psi(DA^*)$).

electron-rich ethylenic moiety in **4**, or a sulfide in **5**, **6**, **7**, **8**, and **9**) and an electronegatively substituted ethylenic group as an electron acceptor. These chromophoric groups were incorporated in various conformationally well-defined[23] alicyclic frameworks that hold the chromophores apart by stretched arrays of three (**1**–**6**) or even five (**7**–**9**) σ bonds.

Results and Discussion

Absorption Spectra. The absorption spectra of compounds **1**–**11** show only minor solvent polarity dependence. Date in *n*-hexane are compiled in Table I, while some representative spectra are shown in Figure 1.

The donor chromophores incorporated in the present bichromophoric molecules show negligible absorption above 220 nm, whereas the acceptor chromophores show a single strong π–π^* transition in this region indicated by A → A* in Table I. Most bichromophoric molecules, except **3b** and **8c**, display an additional long-wavelength transition not attributable to any of the separate chromophores. The intensity of this transition does not vary with concentration (10^{-2}–10^{-5} M). Furthermore, both a lowering of the donor ionization potential and an increase of the acceptor electron affinity lead to a marked bathochromic shift of this long-wavelength band, which is assigned as an intramolecular CT transition (cf. also next section).

The through-bond nature of the interaction responsible for the appearance of the intramolecular CT absorption is most convincingly demonstrated by its presence in the trans-fused bicyclic system **7c** and its absence in the cis-fused isomer **8c** (cf. Figure 1 and Table I). In both **7c** and **8c** the chromophores are separated by at least five σ bonds. Although the configuration of the cis isomer allows for closer spatial approach of the donor and acceptor groups (thus enhancing TSI if any), only the trans isomer provides the stretched zig-zag alignment of the functional group and interconnecting σ bond orbitals predicted[14] to be required for efficient TBI.

The same arguments apply to the absence of detectable CT absorption for **3** as contrasted by its presence for **1**. The enforced equatorial orientation of the nitrogen lone-pair orbital in **1** allows for efficient TBI with the acceptor π system. In **3** the axial orientation of this lone pair largely disables[28] the TBI, whereas in **2** an intermediate situation apparently prevails.[29] These findings fully corroborate earlier conclusions[5,29] based upon the electronic absorption data of related β-amino ketones. As we have indicated earlier,[19b] the electronic interaction between the chromophores becomes manifest not only from the appearance of CT absorption but also from a combined hypso- and hypochromic effect on the A → A* transition as compared to that in suitable reference systems such as **10** and **11**.

From inspection of Figure 1, it can be seen that the total oscillator strength of the two absorption bands in the bichromophoric systems is practically equal to that of the single A → A* transition in the reference systems. This indicates that the CT transition borrows most of its intensity from the A → A* transition. These phenomena are readily accounted for if allowance is made for a sizable amount of configuration interaction between the pure CT excited configuration (wave function ψ (D^+A^-)) and the locally in A excited configuration (wave function ψ (DA^*)) in a description of the lowest excited states (ψ_1, and ψ_2, respectively) of the bichromophoric systems (cf. Figure 2).

First-order perturbation theory[26,30] requires that the hypsochromic shift of the A → A* transition that results from this configuration interaction be given by eq 1 and that the ratio of

$$\Delta E = \beta_{12}^2/\Delta E_0 \qquad (1)$$

the oscillator strengths of the A → A* transition (f_{AA^*}) and the CT transition (f_{CT}) in the bichromophoric systems be given by eq 2. The latter assumes that f_{CT} is completely derived from

$$f_{CT}/f_{AA^*} = \beta_{12}^2/\Delta E_0^2 = \beta_{12}^2/(2h\nu_{AA^*}^{\text{ref}} - h\nu_{AA^*} - h\nu_{CT})^2 \qquad (2)$$

intensity borrowing, which seems to be a reasonable approximation in view of the constancy of the sum of f_{AA^*} and f_{CT}, and that therefore the ratio of oscillator strengths equals the square of the ratio of mixing coefficients.

Both eq 1 and 2 in principle allow for estimation of the interaction matrix element β_{12}, which couples the CT and locally excited configurations, from the experimental data. However, β_{12} as evaluated via eq 1 critically depends upon the estimated value of ΔE and therefore both upon the influence of any configurational interaction between the zero-order states of D and A, an interaction obviously neglected in the simple scheme of Figure 2, and upon the choice of the reference system. The latter is evident from the slightly different $h\nu_{AA^*}^{\text{ref}}$ values observed upon changing the alicyclic system from **10** to **11** (cf. Table I) and from the slight shift of $h\nu_{AA^*}$ upon introduction of a donor group in a conformation that minimizes TBI (i.e., **3b** vs. **10b**). Thus β_{12} was calculated by applying eq 2, which is only slightly sensitive toward small uncertainties in $h\nu_{AA^*}^{\text{ref}}$, with use of **11** as a reference for **1** and **10** for all other bichromophoric molecules; furthermore, the ratio of oscillator strengths was found to be satisfactorily reproduced by that of the molar extinction coefficients. The β_{12} values thus determined (cf. Table I) range from zero for the noninteracting systems **3b** and **8c** to 0.65 eV in some azaadamantane derivatives (**1**). According to the theory of CT intensity borrowing as developed for *inter*molecular complexes by Murrell et al.,[31] these β_{12} values refer mainly to the interaction between the semilocalized highest occupied orbitals of donor and acceptor.

The common proportionality relation[32] of the overlap integral (S_{ij}) and β_{ij} for two atomic orbitals located on different atoms i and j is given by eq 3.[33] For elements from the first and second

$$\beta_{ij} = \tfrac{1}{2}K(\beta^0_i + \beta^0_j)S_{ij} \qquad (3)$$

row of the periodic table CNDO parametrization[33] sets K at 0.75 if either i or j is a second-row element and at unity otherwise. Furthermore the one-center integral β^0 is given a value of 21, 25, and 18.15 eV for C, N, and S, respectively.[33]

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(23) The indicated conformation of **1** and **11** is unequivocal while that of **7c** was recently confirmed by X-ray analysis.[24] The chair conformation of the monocyclic compounds is evidenced from extensive conformational studies on closely related molecules.[25] The cis-fused system **8c** was subjected[26] to extensive conformational analysis by ^{1}H NMR spectroscopy, which shows it to adopt the "nonsteroidal" conformation indicated rather than the "steroidal" conformation proposed earlier.[19c]

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(25) (a) Lambert, J. B. *Acc. Chem. Res.* **1971**, *4*, 87–94. (b) Hirsch, J. A.; Havinga, E. *J. Org. Chem.* **1976**, *41*, 455–462. (c) Allinger, N. L.; Jindal, S. P. *Ibid.* **1972**, *37*, 1042–1045. (d) Seip, R.; Seip, H. M.; Smith, Z. *J. Mol. Struct.* **1976**, *32*, 279–284. (e) Bernard, M.; Jacques, M. St. *Can. J. Chem.* **1970**, *48*, 3039–3044.

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(27) Closest atom–atom distances between the donor and acceptor groups in **7c** and **8c** are 530[24] and 470 pm, respectively.

(28) Gonbeau, D.; Loudet, M.; Pfister-Gillouzo, G. *Tetrahedron* **1980**, *36*, 381–391.

(29) Cookson, R. C.; Henstock, J.; Hudec, J. *J. Am. Chem. Soc.* **1966**, *88*, 1060–1062.

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(31) Murrell, J. N. *J. Am. Chem. Soc.* **1959**, *81*, 5037–5043. Murrell, J. N. *Q. Rev., Chem. Soc.* **1961**, *15*, 191–206

(32) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 295–311.

(33) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

Table II. Emission Maxima (cm^{-1} × 10^3) of Bichromophoric Systems in Solvents of Increasing Polarity (20 °C; ~10^{-5} M; λ_{exc} = 300 nm) and Calculated Excited-State Dipole Moments (μ_e)

solvent	Δf	1c[b]	4c	5b	5c	6c	6d	7c
cyclohexane	0.101	21.6	27.9	*a*	27.4	28.2	*a*	*a*
carbon tetrachloride	0.117	*d*	26.7	27.0	26.7	26.7	24.7	28.6
di-*n*-butyl ether	0.204	20.1	26.0	*c*	25.6	25.3	*c*	26.3
diethyl ether	0.256	19.5	24.4	*c*	24.4	24.4	*c*	24.1
chloroform	0.254	19.0	23.3	23.8	23.8	24.4	21.0	23.8
2-methyl tetrahydrofuran	0.305	*d*	22.0	22.0	21.7	21.5	*c*	21.5
1,2-dichloroethane	0.324	17.6	21.4	22.5	23.0	22.7	20.2	21.6
acetonitrile	0.387	*d*	*a*	20.0	20.0	19.8	17.4	*a*
μ_e,[e] Debye units		10.5[b]	13.1	(12.7)	12.4	13.0	(12.8)	23.0

[a] No emission observed. [b] Data taken from ref 19a. [c] Emission too weak to allow reliable separation from solvent emission. [d] Not determined. [e] Calculated via eq 4, with e = 500 pm for 7c and e = 400 pm for all others.

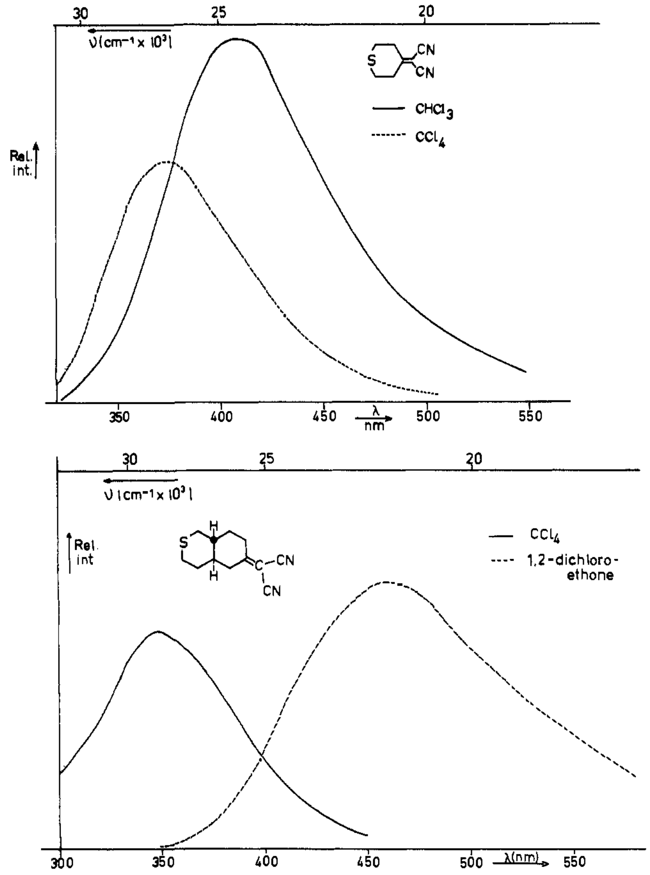

Figure 3. Emission spectra of 6c and 7c in various solvents.

If the β_{12} values compiled in Table I were to result from TSI, formula 3 requires that substantial direct donor–acceptor overlap be involved. Thus according to eq 3, S_{12} values of 0.03, 0.03, and 0.02 are required in **1c**, **6c**, and **7c**, respectively, to explain the observed degree of intensity transfer from the A → A* to the CT transition via a through-space mechanism. In fact, calculated[34] values for direct overlap between the acceptor π system and the donor lone pair are 1 (**1c**, **6c**) to 2 (**7c**) orders of magnitude smaller even if the closest atom–atom distances between donor and acceptor chromophores are implemented in these calculations (i.e., 290 pm,[19a] 310 pm, and 530 pm 24 for **1c**, **6c**, and **7c**, respectively). This once more stresses that TSI contributes to a minor extent, if any, to the overall interaction responsible for the appearance of CT absorption in the present bichromophoric molecules.

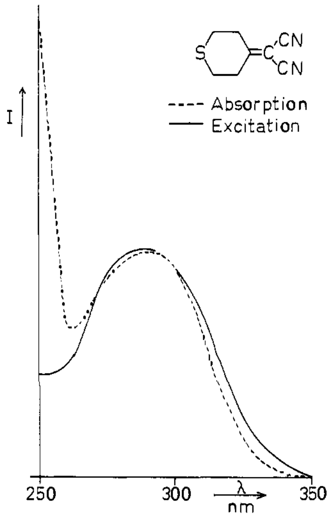

Figure 4. Absorption spectrum (- - -) and corrected excitation spectrum (—) of the CT emission for 6c in 1,2-dichloroethane.

Emission Spectra. The absorptions of the donor chromophores used in the present study lie at too short wavelength to allow their excitation under the conditions employed (λ_{exc} > 250 nm). Furthermore their fluorescence (if any) is expected in the region below 300 nm.

The acceptor chromophores are nonfluorescent presumably because of an extremely rapid radiationless relaxation[36] under concomitant *Z*/*E* isomerization about the ethylenic bond in the excited state reached upon A → A* excitation.

For many bichromophoric systems[37] that exhibit a CT absorption, however, excitation within this absorption ($h\nu_{CT}$) leads to a broad structureless fluorescence (cf. Figure 3 and Table II). The excitation spectrum (cf. Figure 4) of this fluorescence corresponds to the CT absorption ($h\nu_{CT}$), while excitation at shorter wavelengths ($h\nu_{AA}$*) is less efficient. Thus the rapid radiationless deactivation of the locally in A excited state, responsible for the nonfluorescent nature of A, competes effectively with internal conversion to the CT excited state. As expected from its postulated CT nature, which implies a highly polar excited state, the fluorescence of the bichromophoric systems undergoes a large bathochromic shift upon increasing solvent polarity. Under the assumption that the excited-state dipole moment (μ_e) is large as

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[34] Overlap integrals were calculated by using standard parametrization[35] for simple Slater-type orbitals (2p and C and N, 3p on S) with relative orientations corresponding to the π and lone-pair orbitals in molecular models of the bichromophoric systems. It should be noted, however, that also more advanced calculations[28] using a STO-3G basis set confirm the minor contribution of TSI in bifunctional molecules of comparable geometry (i.e., 1,4-piperazine and 1,4-dithian).

[35] (a) Mulliken, R. S.; Reike, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 1248–1267. (b) Boudreaux, E. A.; Cusachs, L. C.; Dureau, L. D. "Numerical Tables of Two-center Overlap Integrals"; W. A. Benjamin Inc.: New York, 1970.

[36] Weiss, R. M.; Warshel, A. *J. Am. Chem. Soc.* **1979**, *101*, 6131–6133.

[37] Fluorescence is most generally provided by those systems that incorporate the 1,1-dicyanoethylene moiety (c) as an acceptor, while the acrylic ester derivatives (a) are mostly nonfluroescent.

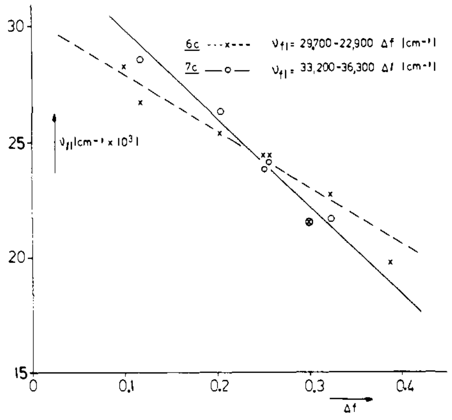

Figure 5. Fluorescence maxima (ν_{fl}) as a function of solvent polarity (Δf) for **6c** (-x-) and for **7c** (-O-).

compared to that of the ground state, relation 4 allows[38] for an estimate of μ_e from a plot of the fluorescence frequency (ν_{fl}) vs. the polarity parameter Δf defined by eq 5.

$$\nu_{fl} = \nu_{fl}(0) - 2\mu_e^2 \Delta f / hce^3 \tag{4}$$

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2) \tag{5}$$

In eq 4 and 5 h is Planck's constant, c the velocity of light, $\nu_{fl}(0)$ the gas-phase position of ν_{fl}, ϵ the solvent dielectric constant, and n the solvent refractive index. Furthermore e denotes the "effective" radius of the solvent shell around the molecule. The latter parameter introduces a large degree of uncertainty. Its value is commonly[38] taken as 40% of the long axis for an approximately ellipsoidal cavity. Plots according to eq 4 for **6c** and **7c** are shown in Figure 5.

For **7c** the slope of the plot is significantly steeper than for **6c**, which according to eq 4 implies a larger value of μ_e for the former compound. By use of the tentative values e = 400 pm 500 pm for compounds in which donor and acceptor groups are separated by three and five σ bonds, respectively, the μ_e values compiled in Table II are calculated. These values correspond to a charge transfer of 75–90%, if the charge separation distance is assumed to be the closest atom–atom distance between the donor and acceptor groups (i.e., ~300 pm in **1–6** and 530 pm in **7**), and thus unequivocally prove the CT nature of these emissions.

Not only the position but also the intensity of the CT fluorescence from the biochromophoric molecules show a large solvent sensitivity (cf. Figure 3). In all cases studied maximum fluorescence quantum yield (ϕ) is found in solvents of intermediate polarity, and a sharp decrease of ϕ is observed both in very polar (i.e., acetonitrile) and in very apolar (i.e., cyclohexane) medium.

Quenching of CT fluorescence in very polar solvents is not unexpected and may readily be accounted[39] for by an increased radiationless decay due to strong and specific interaction between the dipolar excited molecule and the solvent.

In order to probe deeper into the effect of less polar solvents on the relaxation of the CT excited state, we have attempted to determine the relaxation kinetics as a function of solvent by measuring the fluorescence decay via the single photon counting technique. For most of the present bichromophoric systems, however, the fluorescence decay time (τ) was too short (i.e., <200 ps) to allow reliable determination by this technique even though excitation by picosecond pulses was employed (cf. Experimental Section). Only for **4c** well-defined monoexponential decay curves could be measured in a limited number of solvents, as exemplified in Figure 6.

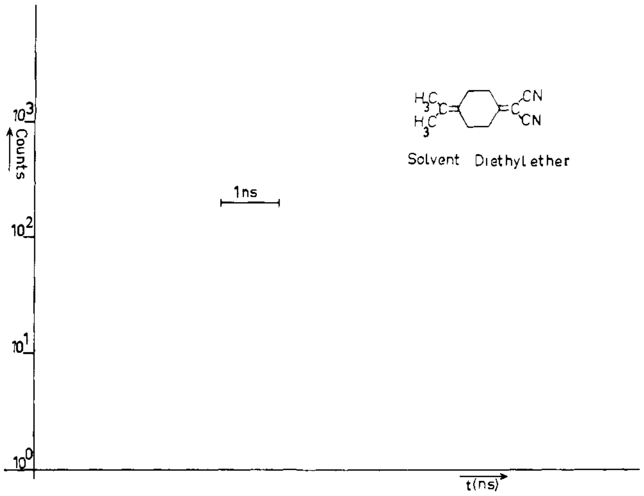

Figure 6. Time-resolved fluorescence decay of **4c** in diethyl ether.

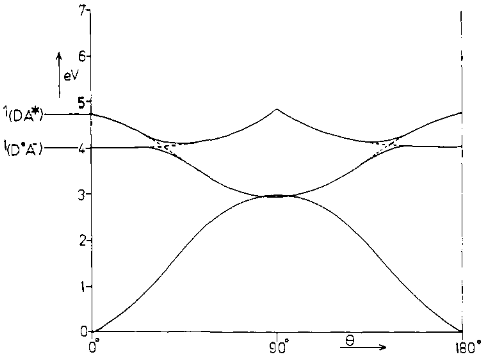

Figure 7. Schematic potential energy profiles as a function of the torsion angle (θ) of the ethylenic acceptor bond for the ground state and for the $^1(D^+A^-)$ and $^1(DA^*)$ states. The curve shapes correspond with those reported for ethylene[43] and its anion radical.[44] The vertical separations at θ = 0° (180°) have been taken to correspond with the spectroscopic transitions in the absorption spectrum of **6c**.

Table III. Photophysical Parameters for the Fluorescence of 4c in Various Solvents (20 °C)

solvent	$\phi \times 10^4$	τ, ns	$\times 10^9 \cdot k_d$, s^{-1}	$\times 10^6 \cdot k_r$, s^{-1}
cyclohexane	3	*b*		
carbon tetrachloride	5	*b*		
di-*n*-butyl ether	18	0.26	3.84	6.9
diethyl ether	50	0.82	1.22	6.1
chloroform	65	1.36	0.73	4.8
2-Me-tetrahydrofuran	32	*b*		
1,2-dichloroethane	85	3.22	0.31	2.6
acetonitrile	<1	*b*		

[a] Calculated via eq 6. [b] Not measurable either due to a very short lifetime or to disturbing solvent emission.

The absolute fluorescence quantum yields of the present systems do not exceed ϕ ~0.01, which allows application of eq 6 to relate ϕ and τ with the radiationless (k_d) and radiative (k_r) relaxation rate constants.

$$\phi = k_r x \tau = k_r/(k_r + k_d) \approx k_r/k_d \tag{6}$$

The data compiled in Table III indicate that both k_r and k_d decrease upon going from solvents of low polarity to solvents of intermediate polarity, the sharper decrease of k_d accounting for the observed increase of ϕ. We tentatively propose this remarkable effect to result from a decrease in the contribution of the locally in A excited state (DA*) to a description of the *emissive* CT state in more polar media.

The configuration interaction model (cf. Figure 2 and eq 1) presented in the preceding section implies such a decrease to occur upon solvent-induced stabilization of the *emissive* CT state relative

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[38] Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183–1184.

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to the Franck–Condon CT state (ΔE_0(emissive) > ΔE_0(FC)).

Thus the decrease of k_r in more polar solvents fully corroborates our conclusion that the CT transition borrows most of its radiative transition probability from the A → A* transition. Furthermore, the nonfluorescent nature of the acceptor chromophores suggests that an efficient radiationless decay channel may become available to the emissive CT excited state as it encroaches the DA* state in the less polar solvents. A very plausible physical mechanism for the latter phenomenon is provided (cf. Figure 7) by torsional vibration about the ethylenic acceptor bond. In the D^+A^- state the force constant of this vibration is expected to be strongly lowered relative to the ground state (DA), as evidenced by the low rotational barrier[40] or even perpendicular orientation[41] reported for ethylenic anion radicals. Thus for small values of ΔE_0 torsional modes of low energy provide an internal conversion from the D^+A^- into the DA* manifold. The latter has a minimum at the perpendicular (θ = 90° in Figure 7) orientation where it very effectively funnels[36,42] into the ground-state potential energy surface.

Concluding Remarks

The alicyclic frameworks in **1**–**9** provide sufficient rigidity to prevent major conformational changes during the excited-state lifetime of these bichromophoric systems. The absence of conformational changes such as a chair → boat transition for the most flexible monocyclic systems is testified by the identical emissive behavior of **6** and its much more rigid bicyclic analogue **5**.

Thus the coupled observation of both CT absorption and CT emission unequivocally proves that these phenomena are not limited to conformations providing direct overlap between the chromophores (TSI), but may also occur for conformations providing effective TBI.

It seems important to stress that although such conformations do not necessarily constitute minima on the ground- or excited-state potential energy surface of bichromophoric systems incorporating simple polymethylene bridges ($M-(CH_2)_n-M'$), they may in principle contribute to spectroscopic properties such as "exciplex" emission and CT absorption of these molecules especially for small values of n. This apparently adds a new dimension to the recent discussions[45,46] of dual exciplex fluorescence and multiexponential emission decay for such bichromophoric systems.

The present study indicates that in addition to the conformational requirements several other factors govern the observability of TBI by electronic absorption and emission spectroscopy. Thus (i) the low energy of the CT state even for large D–A separations allows selective detection and excitation of the CT transition without overlap with local transitions of the individual chromophores. Furthermore (ii) one of the chromophores (i.e., the acceptor) provides a strong local transition of the correct polarization to allow for efficient intensity borrowing by the CT transition. Finally (iii) the relevant molecular orbitals of both D and A have energies and spatial properties that allow effective interaction with the σ orbitals of the interconnecting framework. This regards especially the highest occupied donor and acceptor orbitals (φ_d and φ_a respectively) as evidenced by photoelectron spectroscopy.[47]

As mentioned above interaction between φ_d and φ_a is also in accord with the observation of intensity transfer from the A → A* transition to the CT transition. Extension of the description given by Murrell[31] for intensity borrowing in intermolecular CT systems (i.e., via TSI) to systems involving TBI allows an illuminating visualization of the underlying mechanism of such intensity borrowing.

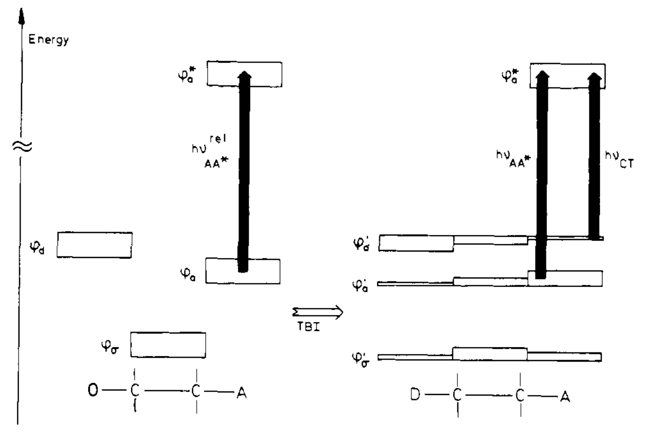
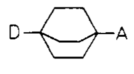


Figure 8. Semilocalized frontier orbital description of the bichromophoric interaction before and after the introduction of TBI between the highest-occupied orbitals of donor and acceptor moieties. Molecular orbitals are represented by rectangles displaced in two dimensions to indicate their relative eneriges and spatial distributions.

Scheme II. Bicyclooctane Derivatives Reported to Show Nonadditive Photophysical Properties



D	A	ref
-NMe$_2$	phenyl	48
1-naphthyl	-COR	49
2-naphthyl	-COR	49

As indicated in the simple frontier orbital diagram of Figure 8, simultaneous interaction of φ_d and φ_a with high-lying σ orbitals (φ_σ) of the interconnecting framework (i.e., TBI) leads to a new set of orbitals (φ_d' and φ_a'), which are (slightly) delocalized over the whole system. This produces a finite transition density between φ_d' and the first vacant acceptor orbital (φ_a^*) even if the latter is assumed to remain completely localized in A.

Although the factors mentioned above are probably essential in producing a discrete optical transition via TBI, other photophysical properties of bichromophoric systems may be strongly modified by TBI without such a transition being detectable in their electronic absorption or emission spectra.

In this relation the recent reports[48,49] concerning unexpectedly efficient intramolecular electron transfer and energy transfer between chromophores separated by the rigid [2.2.2]bicyclooctane unit (Scheme II) should be mentioned. The bicyclooctane unit provides a chromophore separation by five σ bonds that still allows for significant TBI (vide supra), and at least in one case this has explicitly been proposed[49] to account for the photophysical properties of these systems.

Experimental Section

Materials. The preparation and identification of the bichromophoric systems **1**–**9** and the model compounds **10** and **11** have been reported elsewhere (see ref 19a for **1a**–**c** and **11a**–**c**; ref 19b for **3b**, **4c**, **6a**–**c**, and **10a**–**c**; ref 19c for **7c** and **8c**; and ref 26 for **2a**, **5b**–**d**, and **9c**). All solvents used were of the purest grade commercially available.

Apparatus. Electronic absorption and emission spectra were recorded on Cary 17D and SPEX-Fluorolog instruments, respectively. The latter instrument provides options for on-line correction of both excitation and emission spectra. Fluorescence quantum yields were measured relative to quinine sulfate as a standard. Fluorescence decay curves were measured by the single photon counting technique. Excitation was provided by picosecond pulses from a mode-locked frequency-doubled (295.9 nm) Rhodamine-6-G dye laser synchronously pumped by an argon ion laser frequency doubled to 257.25 nm. The time resolution of this system, which has extensively been described elsewhere,[50] is for the moment

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limited by that of the detection photomultiplier (Philips XP-2020) to about 200 ps. Samples for single photon counting were carefully degassed.

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Registry No. 1a, 42949-28-0; **1b**, 42949-26-8; 1c, 42949-32-6; **2a**, 82482-72-2; **2b**, 62702-79-8; **4**, 62702-82-3; **5b**, 82482-73-3; **5**c, 82482-74-4; **6a**, 62702-81-2; **6b**, 10292-84-9; **6**c, 62702-80-1; **6d**, 82482-75-5; **7**c, 63045-23-8; **8**c, 63045-24-9; **9**c, 82482-76-6; **10a**, 40203-74-5; **10b**, 55568-06-4; **10**c, 4354-73-8; **10d**, 3709-25-9; **11**a, 25220-06-8; **11b**, 25694-16-0; **11**c, 36317-36-9.

Nucleophilic Addition to Olefins. 6.[1] Structure–Reactivity Relationships in the Reactions of Substituted Benzylidene Meldrum's Acids with Water, Hydroxide Ion, and Aryl Oxide Ions

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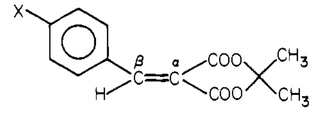
Abstract: The addition of water to *p*-methoxybenzylidene Meldrum's Acid (**1-OMe**), to form an adduct (T_{OH}^-), is subject to weak general base catalysis, just as water addition to carbocations studied by Ritchie. This implies a mechanism in which the base or a second water molecule removes the proton in concert with C–O bond formation. The same mechanism probably applies with the unsubstituted (**1-H**) and the *p*-nitro-substituted benzylidene Meldrum's acid (**1-NO$_2$**) even though general base catalysis was undetectable in these reactions because of experimental difficulties. Rates of water and of hydroxide ion addition to the substituted olefins correlate with σ^+ in the forward and with σ in the reverse direction. This implies an imbalanced transition state in which loss of conjugation is ahead of C–O bond formation. Rates of addition of phenoxide ion to the substituted olefins give a normalized ρ value of 0.56 while the rates of addition of substituted phenoxide ions to **1-NO$_2$** give a normalized $\beta_{nuc} = 0.39$. This result indicates another kind of transition-state imbalance in which negative charge development on the olefin as seen by the substituent in the olefin is larger than that seen by the substituent in the nucleophile. This imbalance can be explained if one assumes that in the transition state part of the negative charge tends to be localized in close proximity to the phenyl group while in the adduct T_{OH}^- the charge is essentially delocalized into the $(COO)_2C(CH_3)_2$ moiety. Our findings are further examples of a growing list of reported transition-state imbalances, and it is suggested that imbalanced transition states are probably the rule rather than the exception for a large variety of reactions. Problems arising from these imbalances in calculating Marcus intrinsic barriers in nucleophilic additions to olefins are discussed. Our data also permit us to estimate a $\rho \approx 1.2$ for the substituent effect on the C–H acidity constant of the carbon protonated OH$^-$ adducts (T_{OH}^0). This unusually high ρ value suggests that in the anion (T_{OH}^-) there is a strong intramolecular hydrogen bond from the OH group to the $(COO)_2C(CH_3)_2$ moiety.

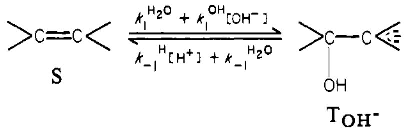
We recently reported a kinetic study of the nucleophilic addition of water, hydroxide ion, and aryl oxide ions to benzylidene Meldrum's acid (**1-H**)[2] and an investigation of the addition of piperidine and morpholine to **1-H**, **1-OMe**, and **1-NMe$_2$**.[3] The results of these studies raised a number of questions which the present and next paper[4] are meant to clarify. They are as follows.



1-H (X = H) 1-NMe$_2$ (X = NMe$_2$)

1-OMe (X = OMe) 1-NO$_2$ (X = NO$_2$)

(1) Hydrolytic cleavage of **1-X**, to form the corresponding benzaldehyde and Meldrum's acid anion, involves the following steps.



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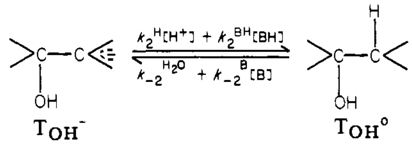
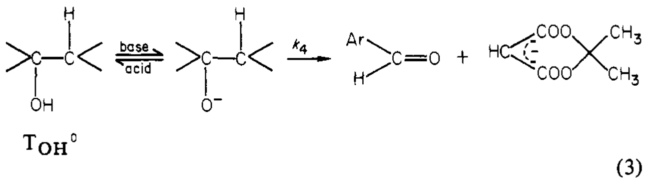


(2)



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