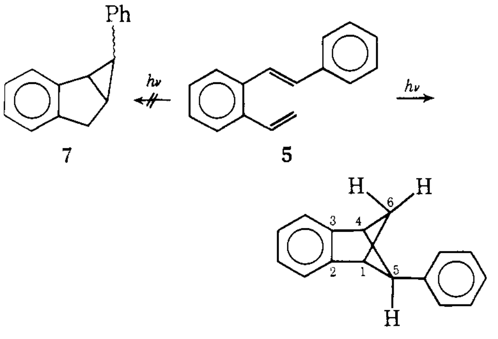
Later on, Meinwald[4] found that 2,3-divinylnaphthalene, but not the 1,2-isomer, does give a small amount (5%) of the [2 + 2] cycloadduct on irradiation.

In the course of our investigations on the photochemistry of stilbene-like compounds, we have found that [2 + 2] cycloaddition is the main reaction on photoexcitation of the phenyl substituted divinylbenzene, 2-vinylstilbene[5] (**5**). Irradiation of a 10^{-3} M solution in hexane at 300 nm under nitrogen in a Rayonet reactor followed by column chromatography of the reaction mixture gave, besides 1-vinylphenanthrene[6] (15%), polymeric products (10%) and traces of two unidentified compounds, 70% *exo*-5-phenylbenzobicyclo[2.1.1]hex-2-ene (**6**, mp 32-33°) and 2% of the corresponding *endo* isomer (mp 88-90°) (eq 2). The absence of



7 **5** **6**

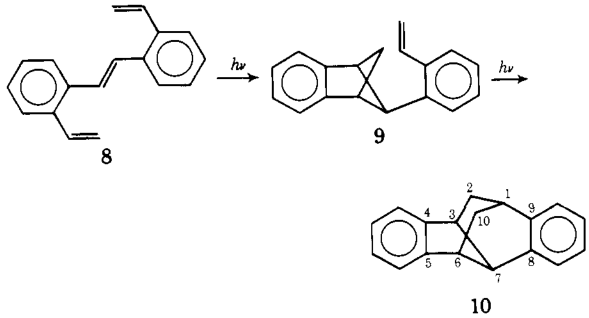
(+endo) (2)

endo- and *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-enes (**7**) in the reaction mixture could be demonstrated by an independent synthesis of these compounds.[7] The occurrence of the isomeric *endo*- and *exo*-4-phenylbenzobicyclo[3.1.0]-hex-2-enes was excluded because of the absence of NMR signals due to methylene protons of a cyclopropane ring (δ 0.0–1.0). The [2 + 2] cycloaddition products were identified on the basis of their spectral data: *exo*-isomer (**6**) mass spectrum *m/e* 206 (M^+, 69%), 91 (100); uv λ_{max} (CH_3OH) 274 nm (log ϵ 3.13), 267 (3.15), 260 (3.09), 254 sh (2.99); NMR (Me_4Si, CCl_4) δ 6.6–7.2 (m, 9 aromatic protons), 3.87 (d, H_{5endo}, $J_{5,6endo} = 7.5$ Hz,[8] $J_{5,6exo} = J_{1,5} = J_{4,5} = 0$), 3.31 (d, H_1 and H_4, $J_{1,6exo} = J_{4,6exo} = 2.5$ Hz, $J_{1,5} = J_{4,5} = J_{1,6endo} = J_{4,6endo} = 0$), 3.07 (doublet of triplets, H_{6exo}, $J_{6endo,6exo} = 6.25$ Hz), 2.32 (doublet of doublets, H_{6endo}); *endo*-isomer mass spectrum *m/e* 206 (M^+, 54%), 91 (100); uv λ_{max} (CH_3OH) 275 nm (log ϵ 2.93), 269 (2.98), 262 (2.90), 256 sh (2.77); NMR (Me_4Si, CCl_4) δ 6.6–7.2 (m, 9 aromatic protons), 4.26 (t, H_{5exo}, $J_{1,5} = J_{4,5} = 2.5$ Hz), 3.44 (t, H_1 and H_4, $J_{1,6exo} = J_{4,6exo} = 0$), 2.66 (doublet of triplets, H_{6exo}, $J_{6exo,6endo} = 5.5$ Hz), 2.35 (d, H_{6endo}). Reduction with H_2 on Pd/C of this compound yielded 1-benzylindane as can be expected for **6.** It excludes that the photoproducts are 5-phenylbenzobicyclo[2.2.0]hex-2-enes.

The cycloaddition occurs in the singlet excited state of **5,** since the triplet sensitizer benzophenone does not convert **5** into **6.** *cis*- and *trans*-**5** give nearly the same product ratio. In both cases the sterically more favorable *exo* product **6** strongly predominates over the *endo* isomer.

The remarkable difference in photochemical behavior between **1** and **5** may be ascribed, at least in part to conformational differences. In the rather rigid stilbene moiety of **5** the vinyl substituted phenyl group has been twisted out of a planar conformation by about 30°.[9] Due to this the olefinic bonds may be nearly perpendicular to each other at least in the *cis* isomer, according to models. However, it is not yet known if the reaction is a concerted process and to what extent the electronic properties of the phenyl substituent may be of influence. It is improbable, however, that the different photoreactivity is caused by differences in bond order of the central bond in the relevant hexatriene moieties of *o*-divinyl aromatics as has previously been suggested.[1b] A further study of the influence of conformational factors on the photochemistry of this type of molecules is in progress.

The [2 + 2] cycloaddition observed for **5** could be used for the synthesis of a new tricyclic $C_{10}H_{12}$ system (**10**). Brief irradiation of 2,2′-divinylstilbene (**8**) gave a [2 + 2] cycloadduct (**9**) similar to **5.** On further irradiation it underwent a $\pi 2 + \sigma 2$ cyclization giving dibenzotricyclo-[4.3.1.0^{3,7}]deca-4,8-diene (**10**, mp 157-158°) in 70% yield (eq 3). The structure given is based on the following spectral data: mass spectrum *m/e* 232 (M^+, 100%); uv λ_{max} (CH_3OH) 264 nm (log ϵ, 4.19), 258 (4.29), 251 (4.19), 246 sh (4.00), 239 sh (3.75); NMR (Me_4Si, CCl_4) δ 6.98–7.35 (symmetrical multiplet, 8 aromatic protons), 3.72 (t, H_7, $J_{6,7}$, $J_{3,7} = 4.5$ Hz), 3.14 (q, H_1, $J_{1,2} = J_{1,2'} = J_{1,10} = J_{1,10'} = 2.9$ Hz), 2.82 (m, H_3 and H_6, $J_{2,3} = J_{61,0} = 1.5$ Hz, $J_{2',3} = J_{6,10'} = 9.0$ Hz), 1.95–1.40 (m, H_2, $H_{2'}$, H_{10}, $H_{10'}$, $J_{2,2'} = J_{10,10'} = 12$ Hz).



8 **9** **10**

(3)

References and Notes

(1) (a) M. Pomerantz, *J. Am. Chem. Soc.*, **89**, 694 (1967); (b) M. Pomerantz and G. W. Gruber, *ibid.*, **93**, 6615 (1971).

(2) J. Meinwald and P. H. Mazzochi, *J. Am. Chem. Soc.*, **89**, 696 (1967).

(3) J. Meinwald and D. A. Seeley, *Tetrahedron Lett.*, 3739, 3743 (1970); L. Ulrich, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **53**, 1223 (1970); H. Heimgartner, L. Ulrich, H. J. Hansen, and M. Schmid, *ibid.*, **54**, 2313 (1971).

(4) J. Meinwald, J. W. Young, E. J. Walsh, and A. Courtin, *Pure Appl. Chem.*, **24**, 509 (1970).

(5) *trans*-2-Vinylstilbene (**5**) was synthesized by a Wittig synthesis using the triphenylphosponium salt of 2-bromomethylstilbene and formaldehyde.

(6) 1-Vinylphenanthrene was identified by an independent synthesis starting from 1-methylphenanthrene.

(7) The *exo* isomer was synthesized according to M. Popovici, V. Ioan, M. Elian, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **12**, 583 (1967). The *endo* isomer was prepared in an analogous way starting with 2-carboxy-*cis*-stilbene.

(8) Long range coupling in this kind of bicyclic compounds is well known. See M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966); K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

(9) Though no data are available for (**5**), the value may be assumed to be nearly the same as for 2,2′-diethylstilbene; see W. H. Laarhoven, R. J. F. Nivard, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **79**, 1153 (1960).

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On the "Utilization of Excited State p*K*'s to Initiate a Ground State Chemical Reaction"

Sir:

A recent communication by Saeva and Olin[1] concludes by stating that "we have demonstrated an excited state acid catalyzed bimolecular reaction." The authors claim to have demonstrated the first photochemical reaction that takes advantage of the increased acidity of phenols in the lowest excited singlet state, one of many important discoveries of the late Professor Theodor Förster. This paper presents some elementary considerations which make the authors' conclusions difficult to accept, and I would venture to say, likely to be indefensible.

The photochemical reaction is the nitrosation, in the 1-position, of 2-naphthol in a buffered (pH 7.0) aqueous solution, a process which is reported to occur only on irradiation and to have a quantum yield of 10^{-4}. The authors believe that the concentration of nitrous acid is a crucial factor and that this is increased by irradiating the naphthol which is a much stronger acid ($\Delta pK_a \sim 6$) in the excited singlet state. The nitrosation is said to involve the reaction of ground-state 2-naphthol with nitrous acid.

Let us consider first the maximum change in the nitrous acid concentration that could possibly be photochemically induced. The aqueous solution is buffered (phosphate) at pH 7.0; the nitrite is initially present at 10^{-3} M. The ionization constant of $HNO_2 = 4.6 \times 10^{-4}$ and the concentration of HNO_2, due to the normal hydrolysis of NO_2^-, is then calculated to be 2.2×10^{-7} M.

The light flux in a Rayonet reactor equipped with 3000-Å lamps is given by the manufacturer as 4×10^{17} quanta cm^{-3} min^{-1}; this is 7×10^{15} photons cm^{-3} s^{-1} or 4.7×10^{-3} J cm^{-3} s^{-1}. The optical density of the solution, using the published absorption spectrum,[2] should be about 1 cm^{-1}. Let us assume that the flux is actually much larger (~200×), or 1 J cm^{-3} s^{-1}, and that it is absorbed in a 1-cm path. Now, using the published lifetime for 2-naphthol (ethanol solution) of $\sim 10^{-8}$ s,[2,3] making the usual steady-state assumption, and assuming that every excited naphthol molecule ionizes, we calculate that the steady-state concentration of photochemically produced protons, and hence HNO_2 molecules according to the authors, is 1.5×10^{10} cm^{-3} or 2.5×10^{-11} M. We have previously calculated that $[HNO_2]$ at pH 7.0 is 2.2×10^{-7} M. It is obvious that even under the very large light flux we have assumed the photochemical perturbation of the nitrous acid concentration would be infinitesimal and could not possibly explain the experimental result.

There is another important nonphotochemical point that should be noted. The reaction was carried out in a buffered solution and the authors state that it is possible to change the microscopic acidity of the solution by irradiation. Proton-transfer reactions of oxygen bases in water are among the fastest known chemical processes, and there is no reason to believe that the buffer present at moderate concentration would not function effectively on the nanosecond time scale to maintain the pH at its normal value. In fact, in fluorescence studies of excited-state acidity, buffers are frequently used to fix the solution pH so that the relative amounts of phenol and phenolate ions can be determined as a function of pH, thus making it possible to measure the pK_a^*. The rate of establishment of the excited-acid-base equilibrium becomes an important consideration at low buffer concentrations ($< \sim 10^{-3}$ M). This area has been studied extensively by Weller[4,5] and much of it has been summarized by Parker.[6] The proton-transfer rates in the naphthol-phosphate system would appear to be more than fast enough to allow equilibrium to be established. If there is a slow step, it is probably the ionization of the naphthol which would result in fluorescence (or reaction) from the un-ionized form. Further, we are asked to believe that the nitrite ion (10^{-3} M) is responsible for deprotonation of the excited naphthol when the sum of the concentrations of $H_2PO_4^-$ and HPO_4^{2-} in a standard phosphate buffer of pH 7.0 is 0.05 M, 50 times as high as the nitrite concentration. However, this line of argument is not worth pursuing further in view of the finding that the change in $[HNO_2]$ caused by irradiation could only be 0.01% of its normal concentration.

There are more questions that could be raised but they are not as important as the elementary ones discussed above. The basic point is that the interpretation of any photochemical reaction having a quantum yield of 10^{-4} should be made with at least a modest degree of caution, and that attractive, elegant mechanisms cannot be proposed simply on the basis of esthetic merit. It would indeed be very nice to find some chemical consequences of Förster's discovery but this search is severely hampered by the short lifetimes of excited singlet states.

References and Notes

(1) F. D. Saeva and G. R. Olin, *J. Am. Chem. Soc.*, **97**, 5631 (1975).
(2) I. B. Berlman, "Handbook of Fluorescence Spectra of Organic Molecules", 2d ed, Academic Press, New York, N.Y., 1971, p 339.
(3) Note that the fluorescence decay rate is the slowest decay rate that can be used in the calculation. Chemical processes, especially ionization in a solution which will support general-base catalysis, will only serve to decrease the excited state lifetime.
(4) A. Weller, *Trans Faraday Soc.*, **27**, 28 (1959).
(5) A. Weller, *Prog. React. Kinet.*, **1**, 189 (1961).
(6) C. A. Parker, "Photoluminescence of Solutions", Elsevier, London, 1968, p 328 ff.

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Molecular Mechanics of the Ferroelectric to Paraelectric Phase Transition in $LiTaO_3$ via Optical Second Harmonic Generation

Sir:

We report the first use of optical second harmonic generation (SHG) as a technique for determining the molecular structure and mechanics of the phase transition in an octahedrally coordinated system, ferroelectric lithium tantalate.

We relate the bulk SHG coefficient d_{333} to the microscopic Ta-O bond hyperpolarizability β_{lmn} via[1]

$$d_{ijk} = \frac{1}{V} A_{il} A_{\mathrm{jm}} A_{\mathrm{kn}} \beta_{lmn} \qquad (1)$$

where the 3 × 3 matrix A represents the transformation from our microscopic (bond) coordinate system into our macroscopic (crystal) coordinate system and V represents the volume of the unit cell. We assume here that the temperature dependence of A is much greater than that of β, i.e. ($\partial A/\partial T \gg \partial\beta/\partial T$), hence any changes in d vs. temperature can be attributed to changes in A.

In a regular octahedron (Figure 1) the acute angle θ_1 between the top set of Ta-O bonds and the C_3 axis is 54.73° and the obtuse angle θ_2 between the other three Ta-O bonds and the C_3 axis is 125.27°, i.e. ($\theta_2 = 180° - \theta_1$). In our trigonally distorted octahedron ($LiTaO_3$, $R3c$, six molecules per cell[2]), we shall use ϕ to measure the deviation of θ_1 and θ_2 from ideality, viz.,

$$\phi \equiv \theta_1 - 54.73° = \theta_2 - 125.27° \qquad (2)$$

This relation mimics the rigorous space group operations ($R3c$) over the expected range of deformation angles, i.e., $0 \leq \phi \leq 6°$. Expanding eq 1 in terms of θ we find

$$d_{333} = \frac{\beta^{\parallel}}{V}(18 \cos^3 \theta_1 + 18 \cos^3 \theta_2) \qquad (3)$$

where the 36 Ta-O bonds per unit cell are divided into two types, 18 with positive direction cosines ($\cos^3 \theta_1$) and 18 with negative direction cosines ($\cos^3 \theta_2$). The $\beta^{\parallel}$ term repre-