$$S \rightarrow {}^1S^* \tag{I}$$

$$ {}^1S^* \rightarrow {}^3S^* \tag{II}$$

$$ {}^3S^* \rightarrow S \tag{III}$$

$$ {}^3S^* + N \xrightarrow{k_d} S + {}^3N^* \tag{IV}$$

$$ {}^3N^* \xrightarrow{k_r} Q \tag{V}$$

tribute the adverse pressure effect to diffusion-controlled competition between steps III and IV. Indeed, the rate constant for the energy transfer process can be expressed in terms of the Debye equation

$$k_d = 8RT/3000\eta \tag{2}$$

where η is the viscosity. This equation is usually employed for viscous solvents such as glycerin, but it has been applied to nonviscous solvents like hexane ($\eta = 0.3cp$ at 25 °C) as well; for instance, Dubois and Van Hemert[7] evaluated first excited singlet lifetimes of naphthalene and benzene derivatives in n-hexane this way in spite of the low viscosity. At 30 °C, the viscosity of toluene increases experimentally with pressure to 150 MPa,[8] and a value for ΔV^*_d can be estimated from these data: it equals +17 cm^3 mol^{-1}. The two volume terms are therefore equal within the margin of error of ± 2 cm^3 mol^{-1}, and diffusion control is strongly implicated. Nevertheless, the inference that step IV is rate controlled is wrong: since $k_d \approx 10^{10}$ M^{-1} s^{-1}, the lifetime of the triplet $\tau({}^3S^*) \approx 10^{-6}$ s in deoxygenated solutions, and [N] $\approx$ 0.2 mol kg^{-1}, the fraction of ${}^3S^*$ quenched by N must be very close to unity.

The key feature is this experiment is of course the high concentration of S. The toluene cut-off occurs at about 270 nm; at longer wavelengths, the extinction coefficient of S averages[9] about 60 at the main emission lines of the mercury source (313 and 366 nm). We furthermore found the absorption spectrum of S to be unaffected by pressure. With a concentration of S at 0.22 mol kg^{-1}, virtually all of the useful light is absorbed in the first millimeter or so, and the N in the bulk of the solution must diffuse into this thin layer in order to be sensitized. Indeed, in experiments in which this concentration was lowered to about 0.001 mol kg^{-1}, the pressure dependence of the pseudo rate constant vanished.

A final word about the reaction volume, found as the difference between $\bar{V}_Q$ (94.9) and $\bar{V}_N$ (102.6) to be about -8 cm^3 mol^{-1}. This net contraction is not reflected in an enhanced conversion rate under pressure. Since molecular shapes and dipoles are not affected significantly by such modest pressures,[10] absorption spectra generally do not change very much.[11] The chemical bonds in the excited state are usually somewhat longer than in the ground state, and there are polarity changes in many instances as well. These changes are at the basis of Ubbelohde's proposal[12] that hydrostatic pressure may well affect the reactions of photoexcited molecules much more than thermal processes; however, this suggestion has thus far not been borne out experimentally. The reason for this is probably that it essentially ignores the Franck–Condon factor: the changes in volume *follow* the absorption step. It may be assumed that the overall volume decrease in the present instance arises during the rapid and irreversible cascading steps and the effect of pressure on these steps is not revealed by the pseudo kinetics.

In conclusion, we have shown by means of the sensitized photoconversion of norbornadiene into quadricyclane under high pressure that the diffusion control often observed in such experiments may be ascribable to macroscopic diffusion rather than to impeded motion at the molecular level.

Acknowledgment. K. Tamura acknowledges a Grant-in-Aid for Science Research from the Ministry of Education, Science and Culture. W. le Noble thanks the NSF for financial support and Dr. H.-D. Brauer (Frankfurt) for correspondence.

Registry No. Norbornadiene, 121-46-0; quadricyclane, 278-06-8; benzophenone, 119-61-9.

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[7] Dubois, J. T.; Van Hemert, P. L. *J. Chem. Phys.* **1964**, *40*, 923.

[8] Bridgman, P. W. "The Physics of High Pressure"; Dover Publications, Inc.: New York, 1970; p 344.

[9] Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 3.

[10] Benson, S. W.; Berson, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 259.

[11] Hamann, S. D.; Linton, M. *Aust. J. Chem.* **1975**, *28*, 701.

[12] Ubbelohde, A. R. *Nature (London)* **1966**, *209*, 28.

Electric Second Hyperpolarizability as a Novel Probe to the Stability of Dianions. Case Study: Four Conformers of $C_6H_8{}^{2-}$

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Received March 12, 1984

The main question which is addressed in this paper is the effect of changes in shape of a molecular anion on its electric response to the environment, with particular reference to its stability. This is an important problem because it is known that the interactions of an anion with its environment (e.g., the solvent) control the chemistry of anionic species.[1,2]

In this computational study we have chosen four isomers of $C_6H_8{}^{2-}$, all of which have been prepared[3-6] and their relative stabilities reported.[6] We also provide evidence for a factor which contributes to the lower stability of the "linear" dianion **2** (Figure 1), in comparison to **1**, as shown by experiment. It is noted that the problem of relative stability of cross and linearly conjugated dianions has been subjected to considerable theoretical and experimental research.[3,6-10] Here a novel point of view is contributed to this discussion.

The response of a molecular anion to its environment is monitored by the average electric polarizability, α, and the second hyperpolarizability, γ.[11,12] Several authors have

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[1] Stevenson, G. R.; Pourlan, M. *J. Phys. Chem.* **1982**, *86*, 1871.

[2] (a) Brauman, J. L.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986. (b) Waite, J.; Papadopoulos, M. G. *J. Mol. Struct.* **1984**, *108*, 247.

[3] Bates, R. B.; Hess, B. A.; Ogle, C. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052.

[4] Bahl, J. J.; Bates, R. B.; Gordon, B., III. *J. Org. Chem.* **1979**, *44*, 2290.

[5] Bates, R. B.; Beavers, W. A.; Greene, M. G.; Klein, J. H. *J. Am. Chem. Soc.* **1974**, *96*, 5640.

[6] Inagaki, S.; Kawata, H.; Hirabayashi, Y. *J. Org. Chem.* **1983**, *48*, 2928.

[7] Rusinko, A., III; Mills, N. S.; Morse, P. *J. Org. Chem.*, **1982**, *47*, 5198.

[8] Clark, T.; Wilhelm, D.; Schleyer, P. v. R. *Tetrahedron. Lett.* **1982**, *23*, 3547.

[9] Inagaki, S.; Hirabayashi, Y. *Chem. Lett.* **1982**, 709.

[10] Gund, P. *J. Chem. Educ.* **1972**, *49*, 100.

[11] Buckingham, A. D.; Orr, B. J. *Q. Rev. Chem. Soc. London* **1967**, *21*, 195.

[12] The first hyperpolarizability, β, being a vectorial quantity, is very sensitive to geometry changes, but it was not considered an appropriate probe for this study since in two of the four cases β is zero by symmetry.

0022-3263/84/1949-3837$01.50/0

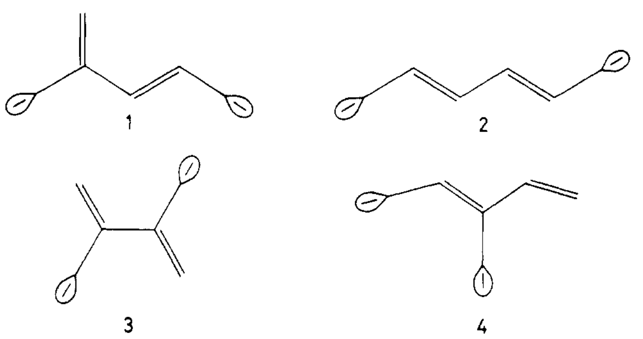

Figure 1. Structures of the isomers of $C_6H_8^{2-}$ which have been studied.

Table I. Calculated Average Polarizability, α, and the Second Hyperpolarizabiity, γ, (in au) of the Four Isomers of $C_6H_8^{2-}$ Considered. Relative Energies (in kcal/mol) Quoted from Ref 6 Are Also Tabulated

			relative energies	
molecule[a]	α[b]	γ[b]	STO-3G[6]	4-31G[6]
1	191	219000	−54.3	−34.8
2	648	−4790000	−52.1	−31.5
3	156	136000	−36.1	−18.5
4	237	348000	0.0	0.0

[a] Geometries of the molecules are from ref 6. The basis set employed is from ref 16. C: 2s (1.325), 2p (1.325). H: 1s (0.8), 2s (0.4), 2p (0.4). [b] Expressions for α and γ are given in ref 14–17.

invoked polarization mechanisms to interpret acidity trends, electronic and IR spectra, etc. (ref 13 and articles cited therein). However, the treatment presented here employs both polarizabilities and hyperpolarizabilities in the analysis of the anionic charge cloud's behavior; an extension which was very recently introduced.[14] The constants α and γ are computed by the CHF-PT-EB-CNDO method, the reliability of which has been established.[14–17] Further, since the character of this study is essentially comparative, any errors in the absolute values of these computed properties are not likely to change the conclusions. Details of the basis set are given in footnote a of Table I. It is worth noting that the accurate experimental measurement of the second hyperpolarizability of ions in solution encounters difficulties due to the environmental interactions which are hard to determine.[2b]

It is seen that the electric field due to the environment stabilizes, in general, the anions as is shown by the polarizabilities.[18] The same trend is also exhibited by the hyperpolarizabilities, with the notable exception of anion **2**, which has a negative value for γ. Further, one observes the pronounced effect of geometry changes on the properties and in particular changes in configuration cause enormous variations in the hyperpolarizability values; the maximum absolute value being associated with the "linear" configuration (anion **2**). These results may be rationalized by the following argument. $C_6H_8^{2-}$ can be considered as a set of interacting segments.[19] The total (effective) field at each unit is the sum of the external field plus the field due to the dipole moment induced at the other segments. Now, considering that the effective field is a vectorial quantity, it becomes clear why the overall property depends so extensively on the geometry of the molecule. Further since the "linear" configuration may be considered as having least vectorial cancellations, one qualitatively understands the difference in the properties observed between **2** and the other anions.

An important implication of the present results is that they provide evidence for a route by which the experimentally found lower stability of **2** with respect to **1**, is attained. Although the polarizability term stabilizes dianion **2** more than **1**, it is observed that anion **2** has a large negative value for the hyperpolarizability. Thus this nonlinearity's contribution will reduce (in absolute terms) the energy, while both the linearity and nonlinearity terms will increase the stability of **1**.[20]

It is finally noted that the four examined compounds are isoelectronic, with the same number and type of bonds. The geometry is the only variable. The considerable difference in the hyperpolarizability values illustrates the aptitude of γ to trace small changes in the intramolecular environment (more sensitively than the energy). We bring attention to the point that the deprotonated carbon does not in general correspond to the site of largest negative charge and Figure 1 should be considered as indicating the site of deprotonation and not that of highest charge concentration.[6]

In conclusion the close connection between molecular shape and the magnitude of the stabilizing interactions (the recipient of which is the anion and originates from the environment) has been demonstrated and the importance of the polarization terms illustrated.

Registry No. 1, 64080-78-0; 2, 64080-77-9; 3, 69780-62-7; 4, 78831-99-9.

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(13) Pellerite, M. J.; Brauman, J. I. "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1980; Part A, p 55.

(14) Waite, J.; Papadopoulos, M. G. *J. Comput. Chem.* **1983**, *4*, 578.

(15) Nicolaides, C. A.; Papadopoulos, M. G.; Waite, J. *Theoret. Chim. Acta* **1982**, *61*, 427.

(16) Papadopoulos, M. G.; Waite, J.; Nicolaides, C. A. *J. Chem. Phys.* **1982**, *77*, 2527.

(17) Waite, J.; Papadopoulos, M. G.; Nicolaides, C. A. *J. Chem. Phys.* **1982**, *77*, 2536.

(18) This is seen by considering that the energy, E, of a molecule in the presence of an electric field, F, is given by[11]

$$E(F) = E^\circ - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \frac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta \ldots$$

The symbols have their usual meaning (ref 11).

(19) Buckingham, A. D.; Sutter, H. *J. Chem. Phys.* **1976**, *64*, 364.

(20) It is noted that the order defined by the relative stabilities is completely different from that defined by the electric properties. This observation may be considered as an illustration of the different behavior exhibited by the inner and the outer regions of the charge cloud and thus our results are complementary to energy evaluations.

Metabolites of the Marine Pulmonate *Siphonaria australis*

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Received April 23, 1984

Marine pulmonates of the genus *Siphonaria* are air-breathing molluscs that resemble limpets in both form and habits. Nearly all specimens examined to date have contained "polypropionate" metabolites that are believed to be employed in a chemical defense against predators. *Siphonaria diemenensis*,[1] *S. pectinata*,[2] and *S. lessoni*[3] all contained α-pyrones exemplified by diemenensin A (**I**). Denticulatin A (**2**), a more complex cyclic hemiketal, was

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(1) Hochlowski, J. E.; Faulkner, D. J. *Tetrahedron Lett.* **1983**, *24*, 1917.

(2) Biskupiak, J. E.; Ireland, C. M. *Tetrahedron Lett.* **1983**, *24*, 3055.

(3) Capon, R. J.; Faulkner, D. J. *J. Org. Chem.* **1984**, *49*, 2506.