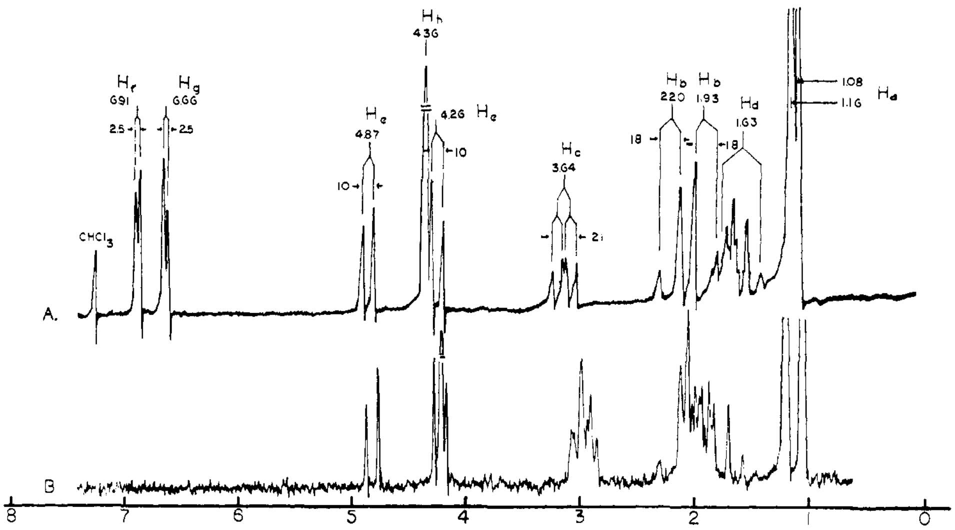


Figure 1. 100-Mc nmr spectra of fomannosin (A) and dihydrofomannosin (B). Chemical shifts are expressed in parts per million from tetramethylsilane and the coupling constants are given in cycles per second. The hydroxyl hydrogen has been exchanged with deuterium oxide to simplify the spectra.

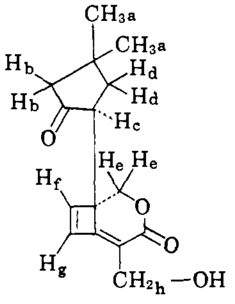
tion of the acetate. The chemical shift of this signal, coupled with its absence in the nmr spectrum of the tetrahydro derivative, suggested that the alcohol was allylic even though attempts to oxidize it with manganese dioxide failed.

The structure of dihydrofomannosin was determined by X-ray crystallographic analysis of its *p*-bromobenzoylurethan derivative ($C_{23}H_{24}BrNO_6$),[3] mp 183–186°.

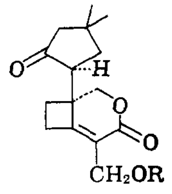
Dihydrofomannosin *p*-bromobenzoylurethan crystallizes in the monoclinic system, space group $P2_1$, with two molecules of $C_{23}H_{24}BrNO_6$ in a cell of dimensions a = 11.57, b = 6.05, c = 15.78 A, β = 95° 35′. Three-dimensional X-ray intensity data were recorded on equiinclination Weissenberg photographs and visually estimated; in all 1610 $[F_o]$ values were obtained.

The initial position of the bromine atom was determined from the three-dimensional Patterson synthesis and the other atoms, apart from hydrogen, were then located by evaluating three-dimensional electron-density distributions with Fourier coefficients weighted according to the method proposed by Sim.[4] The atomic coordinates and temperature factors (anisotropic for the bromine atom, isotropic for the remainder) were then refined by the method of least squares. The present value of R is 11.4%.

The results establish that the *p*-bromobenzoylurethan has structure and relative stereochemistry II (R = $CONHCOC_6H_4$-*p*-Br), and it therefore follows that dihydrofomannosin has structure II (R = H).



I



II

Fomannosin must therefore have structure I since there is only one position to place the missing double bond which satisfies the spectral and chemical data obtained for I. The diene lactone moiety fits well with the ultraviolet and hydrogenation data as previously mentioned. Furthermore, each proton in I can be unequivocally assigned to a signal in the nmr spectrum of fomannosin, as shown in Figure 1A.

The coupling constant (J = 2.5 cps) between H_f and H_g is consistent with a cyclobutene ring[5] and the chemical shifts of H_g and H_f (δ 6.66 and 6.91 ppm) are readily explained by the fact that they are at the end of an extended conjugation system.

Acknowledgments. We wish to express our appreciation to Dr. R. T. Sherwood and Dr. P. B. Hamilton for supplying us with *Fomes annosus* extracts and to Dr. C. G. Moreland for obtaining the 100-Mc nmr spectra for us. This investigation was supported in part by a grant from the National Science Foundation (GB 2878).

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[4] G. A. Sim, *Acta Cryst.*, **12**, 813 (1959); **13**, 511 (1960); "Computing Methods and the Phase Problem in X-ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, Oxford, 1961, p 227.

[5] (a) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963); (b) G. V. Smith and H. Briloff, *ibid.*, **85**, 2016 (1963); (c) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

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The Thermal *cis–trans* Isomerization of Diimide. A Theoretical Study

Sir:

Recent spectroscopic investigations on the structure of diimide[1,2] have prompted us to study the *cis–trans*

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[1] E. J. Blau and B. F. Hochheimer, *J. Chem. Phys.*, **41**, 1174 (1964).

[2] K. Rosengren and G. C. Pimentel, *ibid.*, **43**, 507 (1965).

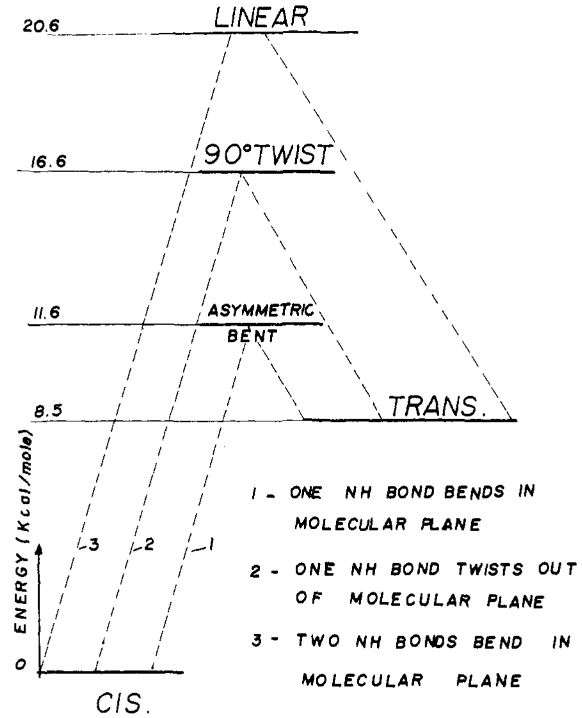

Figure 1. Energies of the various configurations of diimide.

thermal isomerization of the molecule. Tentatively, we have used the extended Hückel method in its plainest form, devised by Hoffmann.[3] The following possible activated complexes have been considered: (1) an asymmetric bent structure in which one NNH angle is 180° whereas the other is allowed to optimize (*i.e.*, it takes on whatever value leads to the most stable configuration); (2) a 90° twisted structure in which an NH bond is twisted about the NN axis while both NNH angles are allowed to optimize; and (3) the linear structure.

For the diagonal elements of the Hamiltonian matrix, the following valence-state ionization potentials (ev) for hydrogen and nitrogen have been used: H_{ii}(H1s) = −13.6, H_{ii}(N2s) = −25.58, H_{ii}(N2p) = −13.94. The last two values correspond, respectively, to the ionization processes $s^2ppp \rightarrow sppp$ and $s^2ppp \rightarrow s^2pp$.[4] The nondiagonal elements H_{ij} have been calculated by means of the Wolfsberg–Helmholtz formula[5]

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$$

where $S_{ij} = \int \chi_i^* \chi_j d\tau$ and K has been given the value 1.75.

The NN and NH bond distances have been assumed to remain constant and equal to 1.22 and 1.03 A, respectively, throughout the distortions. These values represent averages of the best bond-distance data available on a few related molecules.[6] Minimization of the energy provided the following values for the optimum NNH angle: 128° in the *cis*, *trans*, and asymmetric bent geometries and 143° in the 90° twisted structure. The corresponding energies relative to the *cis* molecule, including the energy of the linear structure, are given in Figure 1. In view of the approximate nature of the treatment, the results presented in Figure 1 should not be taken in a strict quantitative sense. A refinement we are considering to introduce in the method would consist in varying the Hamiltonian matrix elements according to the atomic charges in the molecule.

The infrared spectrum of the species had been first explained in terms of the *cis*-bent configuration.[1] A more recent and more detailed study,[2] however, interprets the spectrum as being due primarily to the *trans*-bent form, with a few bands attributable to the *cis* form. It is seen that the calculations predict the *cis* molecule to be more stable than the *trans*. It is not impossible that the procedure is in error on this point. Recent nonempirical calculations predict the *trans* molecule to be the more stable one.[7] Experimentally, the relative stabilities of *cis*- and *trans*-diimide have not yet been established.

It is also noticed from Figure 1 that the average energy required to proceed from *cis* and *trans* through the linear form is approximately twice the average activation energy for the process going through the asymmetric bent form. This is, of course, quite reasonable. However, in an independent electron treatment like the one performed here, there is some uncertainty as to the relative energy of the linear form. As a consequence of the spacial degeneracy characterizing the linear configuration, there actually correspond several distinct electronic states to the level indicated in the figure. The Hückel treatment does not make a distinction between these various states.

In an earlier calculation, based essentially on a simplified Hückel-type procedure, Wheland and Chen[8] computed for the optimum angle of the asymmetric bent form the surprisingly low value of 76°, whereas the present calculation provides a much more plausible value of 128°.

The levels of the figure suggest the following further remarks. (1) The various activation energies are remarkably low. The small amount of energy required to bring the molecule into its linear form implies quite a shallow potential curve; this may be related with the great ease of simultaneous *cis* addition of the hydrogens to a variety of symmetric multiple bonds of different lengths, *e.g.*, $-N{=}N-$, $>C{=}C<$, $-C{\equiv}C-$, and $O{=}O$.[9]

(2) The activation energy for the isomerization (pathway 1) is found to be much lower than for the corresponding reaction in N_2F_2, where the activation energy has been recently found experimentally equal to 32 kcal/mole.[10] However, if in both molecules the process involves the bending of the NNF or NNH angles, it should not be surprising that the potential surface is shallower in N_2H_2. As a comparison, the sharp drop in bending force constant observed when passing from NF_3 to NH_3 (1.92 to 0.64 × 10^5 dynes/cm[11,12]) should be mentioned.

(3) It may seem peculiar that the energy of the 90° twisted form lies so low. It had been supposed pre-

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(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(4) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962); see also footnote 39 in this paper.

(5) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

(6) L. E. Sutton, "Tables of Interatomic Distances etc.," Special Publication No. 11 and Supplement, The Chemical Society, London, 1958, 1960.

(7) L. C. Allen, private communication; L. J. Schaad, private communication.

(8) G. W. Wheland and P. S. K. Chen, *J. Chem. Phys.*, **24**, 67 (1956).

(9) S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem.*, **4**, 271 (1965).

(10) J. Binenboym, A. Burcat, A. Lifshitz, and J. Shamir, *J. Am. Chem. Soc.*, **88**, 5039 (1966).

(11) P. N. Schatz and I. W. Lewin, *J. Chem. Phys.*, **29**, 481 (1958).

(12) W. T. King, *ibid.*, **36**, 165 (1962).

viously[8,10] that the twisted form would involve a decoupling of the π electrons and that consequently process 2 would require an activation energy of the order of the barrier height in ethylene, 61 kcal/mole.[13] However, an analysis of the symmetry properties of the two twisted molecules reveals that one deals here with two entirely different cases. In twisted ethylene, as in the planar molecule, the 2pπ orbitals of the carbons do not mix with the orbitals of σ type. When the twist angle is 90°, the π bonding and the π antibonding molecular orbitals become degenerate. In diimide, on the contrary, owing to the different symmetry of the molecule, this degeneracy does not appear. The C_2 point group, to which the twisted molecule belongs, enables the mixing of the 2pπ nitrogen orbitals with the 2s and 2pσ orbitals. The destabilization due to the decrease in π overlap is compensated to a certain extent by the appearance of some σ bonding in the molecular orbital which describes the π bond in the planar molecule.

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(13) B. S. Rabinovitch, J. E. Douglas, and F. S. Looney, *J. Chem. Phys.* 20, 1807 (1952).

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Hydrated Electron Reactions in View of Their Temperature Dependence

Sir:

The rates of reaction of hydrated electrons with hundreds of reactants, organic and inorganic, have been determined,[1,2] and it has been shown that the reactivity of e_{aq}^- toward a series of homologous reactants may be correlated with the electron deficiency of a functional reactive group.[1] It is obvious that any deeper understanding of the nature of e_{aq}^- reactivity requires information on the energy and entropy of activation of these reactions.

The energy of activation of e_{aq}^- reactions has been measured in a limited number of cases;[3-5] moreover, some of the values published are open to criticism. For the $e_{aq}^- + H_3O^+$ reaction ΔE = 3.2 kcal/mole was determined[3] and a comparable value of 3.8 kcal/mole was obtained by another group of investigators.[5] ΔE = 2.0 kcal/mole was estimated[4] for the $e_{aq}^- + C_6H_5CH_2COO^-$ reaction, based on the competition with CCl_3COO^-. This result is most probably erroneous in view of the complications involved in reactions of e_{aq}^- with polyhalo aliphatic compounds.[6] Baxendale, *et al.*,[5] have found ΔE = 4.2 kcal/mole for the $e_{aq}^- + Co(NH_3)_6^{+3}$ reaction and ΔE = 5.7 and 7.7 kcal/mole for the reactions of e_{aq}^- with Co^{+2} and Mn^{+2}, respectively.

We have measured the temperature dependence of a number of reactions of e_{aq}^- with reactants of different chemical nature, the reactivity of which ranges from 3 × 10^5 to 6 × 10^{10} M^{-1} sec^{-1}. The relative rate constants of the different reactants were determined by competition kinetics *vs.* nitrate ions[7] or *p*-bromophenol (PBP). It has been shown that *p*-bromophenol undergoes debromination by e_{aq}^- and by H atoms. In the presence of 0.1 *M* 2-propanol (added as a H-atom scavenger) $G(Br^-) = 2.6 \pm 0.2$ is obtained in deaerated solutions for doses up to 3.7 × 10^8 ev g^{-1} (Co^{60} γ rays, dose rate 3.7 × 10^{17} ev^{-1} g^{-1} min^{-1}). The specific rate constants at 20° were calculated from values of $k_{e_{aq}^-+NO_3^-} = 1.1 \times 10^{10}$ M^{-1} sec^{-1},[3] and $k_{e_{aq}+PBP} = 1.2 \times 10^{10}$ M^{-1} sec^{-1}. From the relative rates measured at 20, 45, and 70°, the difference between the activation energies of the reactants and the reference compounds, $\Delta(\Delta E)$, was calculated. The experimental error amounted to 0.5 kcal/mole.

$\Delta(\Delta E)$ of $e_{aq}^- + H_3O^+$ and $e_{aq}^- + NO_3^-$ was found to be 0.4 ± 0.4 kcal/mole. The corresponding $\Delta(\Delta E)$ of $e_{aq}^- + H_3O^+$ and e_{aq}^- + PBP was 0.0 ± 0.4 kcal/mole. It was concluded that the activation energies of these three reactions are equal within the experimental error. These and other $\Delta(\Delta E)$ determined in this study are summarized in Table I. The values of the specific rate constants obtained agree within the experimental error with the rate constants obtained directly by pulse kinetics. The energies of activation of the different reactions studied, derived from the experimental $\Delta(\Delta E)$ and the measured ΔE of the $e_{aq}^- + H^+$ reaction,[3] range between 3.0 and 3.9 kcal/mole. The specific rates of these reactions range over *five* orders of magnitude, and no correlation whatsoever could be found between ΔE and $k_{e_{aq}^-+X}$. It could be tentatively stated therefore that $e_{aq}^- + X \rightarrow X^-$ reactions have an over-all activation energy of 3.5 ± 0.4 kcal/mole. This value is equal to the activation energy of diffusion in aqueous solution,[8,9] *i.e.*, 3.5 kcal/mole at 45°.[9] This means that e_{aq}^- reactions, irrespective of their specific rates, take place without any energy of activation in excess of the energetic requirements of diffusion. The entropies of activation, $\Delta S^{\ddagger}$, are listed in the last column of Table I.

The statement that all $e_{aq}^- + X \rightarrow X^-$ reactions have $\Delta E \simeq 3.5$ kcal/mole does not exclude the possibility of finding experimental $\Delta E \neq 3.5$ kcal/mole for reactions of e_{aq}^- with certain reactants. This may occur if the $e_{aq}^- + X$ reaction is preceded by a preequilibrium $Y \rightleftarrows X$ where $k_{e_{aq}^-+X}$ differs significantly from $k_{e_{aq}^-+Y}$. Acid–base preequilibria are the best

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(1) M. Anbar in "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p. 55.

(2) For a compilation of data, see M. Anbar and P. Neta, *Intern. J. Appl. Radiation Isotopes*, **16**, 227 (1965); an up-to-date version of this paper is in press.

(3) J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, **68**, 1524 (1964).

(4) M. Anbar and P. Neta, *Chem. Commun.*, 365 (1965).

(5) J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Roy. Soc.* (London), **A286**, 320 (1965).

(6) S. R. Logan and P. B. Wilmot, *Chem. Commun.*, 558 (1966).

(7) A. Appleby, G. Scholes, and M. Simic, *J. Am. Chem. Soc.*, **85**, 3891 (1963).

(8) S. Glasstone, H. Eyring, and J. K. Laidler, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp 505, 523.

(9) H. S. Taylor, *J. Chem. Phys.*, **6**, 331 (1938).