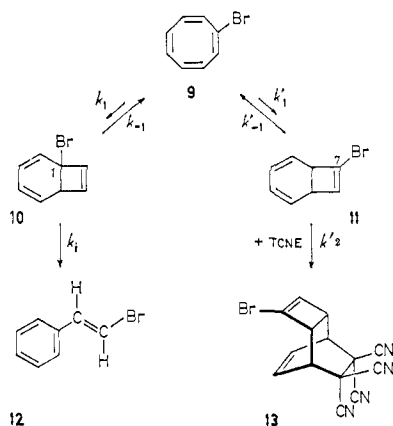


Figure 1. Competition between rearrangement and TCNE addition. Results of Table I are plotted using eq 3.

in the constant ratio of 1:50, were allowed to react in acetonitrile (in this polar solvent k_1 is rate determining for the formation of **12**⁵) in increasing dilution; **12** was



analyzed by glpc using methylnaphthalene as internal standard, and **13** was determined by gravimetry. Table I shows satisfactory total yields and the expected

Table I. Reaction of Bromocyclooctatetraene with TCNE (1:50)^a

[TCNE], mM	% 12 + 13	Mol %		13/12
		12	13	
1914	96	63.5	32.8	0.517
765	99	68.7	30.2	0.440
639	95	66.1	28.6	0.433
383	99	72.0	27.0	0.375
319	95	69.5	25.2	0.363
255	97	73.7	23.5	0.319
191	97	75.0	21.8	0.291

^a In acetonitrile at 70°; competition between rearrangement and adduct formation.

increase of the rearrangement product with decreasing concentration of TCNE.

Applying the steady-state treatment⁵ to **10** and **11**, one obtains

$$\frac{d[\mathbf{12}]}{d[\mathbf{13}]} = \frac{k_1 k_1 (k_{-1}' + k_2' [\text{TCNE}])}{(k_{-1} + k_1) k_1' k_2' [\text{TCNE}]} \quad (1)$$

The 50-fold excess of TCNE makes it possible to use the product ratio instead of the differential quotient; also, assuming $k_{-1} \ll k_1$ in acetonitrile leads to

$$\frac{\% \mathbf{12}}{\% \mathbf{13}} = \frac{1}{Q} = \frac{k_1 (k_{-1}' + k_2' [\text{TCNE}])}{k_1' k_2' [\text{TCNE}]} \quad (2)$$

and after transformation to the equation for a straight line, we have

$$Q = \frac{k_1'}{k_1} - \frac{k_{-1}'}{k_2'} \frac{Q}{[\text{TCNE}]} \quad (3)$$

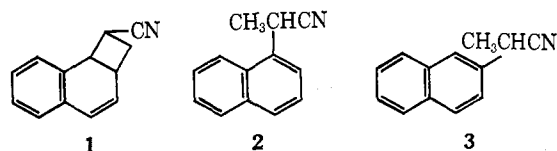
The results of Table I are plotted in Figure 1. From the intercept, $k_1'/k_1 = 0.544$ is calculated. Thus, the tautomerization rate constants of bromocyclooctatetraene to **10** and to **11** are in the ratio 65:35 (acetonitrile, 70°). The absolute value of k_1 has been previously reported.⁵

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Solvent Effects on the Photoaddition of Naphthalene and Acrylonitrile. Evidence for an Exciplex as Intermediate

Sir:

We previously reported that the photoaddition of naphthalene and acrylonitrile in alcohol solution affords cycloaddition products,^{1,2} e.g., **1**, together with naphthylpropionitriles **2** and **3**. We have de-



termined² that the cycloadducts are formed from the lowest singlet excited state of naphthalene. We now wish to report that the formation of the naphthylpropionitriles involves the solvent, acting as a proton source. The proton acceptor is very probably the exciplex of naphthalene singlet and acrylonitrile.

The evidence is as follows. First, it was found that the ratio of cycloaddition:substitution depended on the solvent used, and the ratios for some solvents are given in Table I. While several parameters undoubtedly contribute to the solvent effect, the results show that the fraction of substituted naphthalenes increases with acidity and polarity of the protic medium. It is interesting that neither type of adduct is formed in aprotic solvents, even those with a high dielectric constant, e.g., acetonitrile.

Second, it was shown that the most acidic proton of the solvent is incorporated into the methyl groups of **2** and **3**. Thus, when deuterium acetate ($\text{CH}_3\text{CO}_2\text{D}$) or deuteriomethanol⁸ (CH_3OD) was employed as solvent, the naphthalene derivatives contained one deuterium label in the methyl groups.⁴ The simul-

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(3) We thank Dr. N. H. Werstuck for this material.

(4) Deuterium assay was by nmr and mass spectra.

Table I. Solvent Dependence of Product Distribution in Naphthalene-Acrylonitrile Reaction

Solvent	HCO ₂ H	CH ₃ CO ₂ H	CF ₃ CH ₂ OH	CH ₃ CH ₂ OH	CH ₂ ClCH ₂ OH	CH ₃ OH	CH ₂ CH ₂ OH	(CH ₃) ₂ CHOH	(CH ₃) ₂ COH	CH ₃ CN	Dioxane
Fraction (%) ^a , ^b of substituted naphthalenes (2 + 3)	75	8.8	53.8	29.4	43.2	29.4	7.8	~1	0	0	0
Quantum yield		0.16	0.28	0.26	0.24	0.26	0.28	0.32	0.27	Small	Small
Dielectric constant ^c (pK _s) ^d	58.5 (3.77) ^d	6.15 (4.76) ^d	(12.37) ^e	32.63 (15.5) ^e	25.8 (14.31) ^e	32.63 (15.5) ^e	24.3 (15.9) ^e	18.3 (18.0)	10.9 (19.0)	39.5	2.21

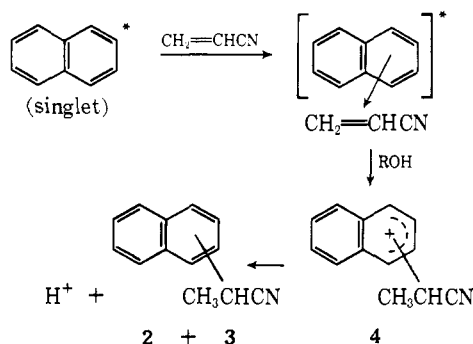
^a Assay was by vpc analysis on 5 ft × 1/8 in. of 5% QF-1 on Chromosorb W at 185°. ^b The balance was the cycloadducts (ref 2) which were stable in all of the solvents. The acrylonitrile was 1 M, and 0.1 M 2,3-dimethyl-1,3-butadiene was added to prevent decomposition of 1, in all runs except formic acid. ^c Taken from National Bureau of Standards Circular 514, "Table of Dielectric Constants of Pure Liquids," U. S. Government Printing Office, Washington, D. C., 1951. ^d J. D. Roberts and M. Casserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964, p 510. ^e P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **82**, 795 (1960).

taneously formed cycloadducts contained no deuterium.

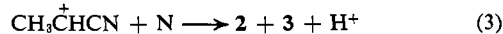
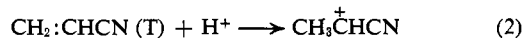
These experiments show that the solvent is acting as a proton source. Therefore, 2 and 3 must be formed either in a termolecular collision of solvent, naphthalene singlet, and acrylonitrile, or by solvent protonation of an exciplex of naphthalene and acrylonitrile. The latter is more probable, in view of the observed quenching² of naphthalene fluorescence by acrylonitrile. The relative singlet energies of acrylonitrile and naphthalene are approximately 133 and 100 kcal (from absorption data), which clearly precludes efficient, exothermic energy transfer, and the quenching must be a result of complexation. We have already reported¹ that there is no detectable charge transfer absorption in naphthalene-acrylonitrile mixtures, which indicates that strong electronic interaction is absent in the ground state.

We propose the mechanism shown in Scheme I. The steps are: (i) formation of a naphthalene-acrylonitrile exciplex; (ii) protonation of this at the CH₂ group;^{5,6} and (iii) collapse of the ion 4 to the naphthylpropionitriles 2 and 3.

Scheme I



An alternative mechanism might consist of sensitization of acrylonitrile by naphthalene (T₂),⁷ protonation of acrylonitrile triplet, and electrophilic attack of the carbonium ion formed on naphthalene. The steps would be as follows.



If this were the mechanism, reaction 4 would certainly compete with product formation in step 3.⁸ However, on photolysis in methanol, no 2-methoxypropionitrile, which is stable under the photolysis conditions, was detected, providing evidence against this mechanism.

(5) Protonations of a σ -bonded, zwitterionic species of a highly reactive ground-state molecule or of an ion pair are also possibilities.

(6) The absence of cycloadducts from the photolysis in acetonitrile suggests that a proton source is necessary for the cycloaddition to occur. A mechanism for this might involve protonation of the exciplex on nitrogen.

(7) Since acetophenone ($E_T = 73$ kcal) and Michler's ketone ($E_T = 61$ kcal) fail to sensitize the reaction, the lowest triplet of naphthalene is not involved. However, T₂ of naphthalene lies below S₁, but above T₁ of acetophenone: R Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

(8) In aqueous acetone, the rate of collapse of a secondary carbonium ion is about 10⁹ sec⁻¹: S. Winstein, *Quart. Rev. Chem. Soc.*, **23**, 141 (1969). In order for a free carbonium ion to react with 0.01 M naphthalene in our experiments, the rate would have to exceed the diffusion limit.

Exciplexes have been proposed as intermediates in photocycloadditions.^{9,10} Our suggestion that an exciplex reacts with solvent seems to be without precedent, although reactions are known which may be related to the naphthalene-acrylonitrile addition. These are the addition of dimethyl acetylenedicarboxylate and naphthalene in methanol to afford naphthyl fumarates,¹¹ and of benzene and maleic anhydride in trifluoroacetic acid, forming phenylsuccinic acid.¹²

We are continuing this work in order both to discover further cases of the interesting substitution and obtain a more precise mechanistic interpretation.

Acknowledgments. We thank the National Research Council of Canada and the Imperial Oil Co. Ltd. for financial support.

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Cyclic Systems Containing Divalent Hydrogen Symmetrically Placed between sp^2 Hybridized Electron-Rich Atoms. A New Form of Chemical Bond?

Sir:

Recent experiments¹⁻⁷ and theories⁸⁻¹¹ relating to anomalous forms of water, alcohols, and acids, and to gas-phase hydrogen fluoride suggest the possible existence of a heretofore unrecognized type of chemical bond. The results given in this letter make direct mathematical and physical connection between Schrödinger's equation and the above-noted research by means of *ab initio* electronic wave functions for water and hydrogen fluoride cyclic polymers constructed with a high-accuracy basis set. Present ability to provide an *a priori* answer to the question posed by this letter's title is essentially pushed to the technical limit by our calculations. In addition to the *ab initio* results, we have made estimates of further corrections beyond the range of directly computable wave functions.

Molecular orbital calculations augmented by configuration interaction were computed on the Princeton

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University IBM 360/91 digital computer with programs developed in this laboratory. The exact nonrelativistic Hamiltonian with clamped nuclei was used and proved to be valid because the charge distributions found are not enough different from known bond types to invoke relativistic effects or a break down of the Born-Oppenheimer approximation. Choice of orbital basis set and estimation of the instantaneous electron-electron correlation energy are the key problems. The orbital basis set employed was sufficient to span the Hartree-Fock atomic limit and this set was used with the molecular Hamiltonian both in LCAO and in a more flexible (extended) representation that lowers the total energy slightly and accommodates the molecular environment by more linear variation coefficients. Previous research on conventional hydrogen-bonded dimers¹² shows that for this type of basis set one can be assured of obtaining the correct relative stability ordering among different geometrical arrangements. (This has likewise been proved *not* to be so for cyclic hexamers with some simpler basis sets.¹³) The question of absolute binding energies for the polymers relative to separated H₂O molecules is more difficult. Although it has long been known that binding energies for strong ordinary bonds computed from molecular orbital solutions close to the Hartree-Fock limit are considerably less than experimental values, a similar rule has not yet been widely established for hydrogen bonding. However, there now exist some very high-accuracy molecular orbital water dimer wave functions for conventional hydrogen bonds^{12,14,15} and the evidence is that hydrogen bond energies follow roughly the same rule as for ordinary bonds and also that radial and angular polarization effects produced on the basis set by the molecular environment largely cancel as far as binding energy estimates are concerned. Thus when used with Hartree-Fock atomic orbitals, the LCAO approximation produces a properly conservative estimate of the binding energy. For hydrogen bonding it underestimates binding energies by perhaps 10-40%. The LC(Hartree-Fock)AO approximation has the further virtues of providing the most meaningful reference point for carrying out configuration interaction and for decomposing the molecular charge distribution into atomic constituents.

We have carried our *ab initio* treatment beyond the molecular orbital level by configuration interaction through the usual and very slowly convergent procedure of adding determinants made from the four lowest lying virtual orbitals. In accord with similar results found for a wide range of molecular systems studied by numerous investigators, the correlation introduced in this manner yields an almost meaninglessly small energy lowering, but it is essentially the limit that can be handled directly by present day computers for the systems considered here.

Our *ab initio* computations are summarized in Table I (for the hydrogen fluoride tetramer an extensive geometry search for the various levels of wave functions was carried out and only the optimized values are

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