enhanced values of the ^{13}C–H coupling constants at positions 2 and 3.[7] It opens up,[12] probably to re-form a similar zwitterion. The activation energy goes up to ΔG^*_{323} = 24.6 kcal mol^{-1} (acetone) in line with the reduced strain in the [2 + 2] adduct, thermodynamically more stable than the [4 + 2] adduct. Again, an increase in the solvent polarity boosts the rate of decomposition of **3** to form irreversibly another $C_{18}H_{14}N_4$ isomer **4**.[13] Superimposed upon the effect of solvent polarity, the effect of solvent nucleophilicity[15] is now conspicuous (Figure 1). To our knowledge, such a nucleophilic solvent effect is unprecedented for these types of reaction. At the lower solvent polarities, a bimolecular pathway k_2 [ether] sets itself in competition against the unimolecular k_1 decomposition *via* the zwitterionic intermediate. Like its predecessor, this [2 + 2] → [2 + 6] step shuns orbital concert.[16] Indeed, rarely are fulvenes accessible to [2 + 6] concerted cycloadditions.[17]

The [2 + 6] adduct proper cannot be isolated. It rearranges smoothly (Scheme I) into the more stable isomeric cyclopentadiene **4**, a process for which now the most likely mechanism is 1,5-hydrogen sigmatropy.[18,19] The corresponding *ca.* 24.3 kcal mol^{-1} energy barrier[19] is easy to overcome without equilibration back to the [2 + 2] adduct; release of the cyclobutane strain in **3** ensures that the **3** → **4** conversion be highly exothermic.

In summary, one witnesses successive changes in the relative orientation of dicyclopropylfulvene and tetracyanoethylene. The TCNE residue moves from its initial position above the face of the fulvene, allowing for maximum overlap and thus producing the fastest rate, to its final resting position in the nodal plane of the fulvene, where strain has been reduced to a minimum. It is rather remarkable that **2** does not transform itself *directly* into **4** *via* a zwitterion stabilized at the negative pole by the cyano substituents and at the positive pole by the resonance inherent both to the pentadienyl cation and to the cyclopropylcarbinyl cation. The full electronic and nuclear reorganizations do not have enough time to be completed before the intermediate zwitterion collapses to the intermediate structure **3**. It is only then, after **3** opens to another, better delocalized, zwitterion that access is gained to the C-6 terminus. In other words, and to quote a referee, both **2** and **3** rearrange *via* formally the same intermediate, yet the mode of generation of the intermediate determines its fate!

Acknowledgment. We thank the Fonds de la Recherche Fondamentale Collective for a grant toward the purchase of the Bruker HFX-90 nmr spectrometer. We thank Professors Anteunis (Gent) and Gaudemer (Gif-Paris) for mass spectra.

References and Notes

(1) Addition modes of cyanoolefins, III; part I, M. Acar, A. Cornélis, and P. Laszlo, *Tetrahedron Lett.*, 3625 (1972); part II, A. Cornélis, P. Laszlo, and C. Pasquet, *ibid.*, 4335 (1973); presented in part at the Journées de Chimie Organique, Orsay, France, Sept 18–20, 1974.

(2) P. Yates, *Advan. Alicyclic Chem.*, **2** (1968).

(3) K. N. Houk, J. K. George, and R. E. Duke, Jr., *Tetrahedron*, **30**, 523 (1974).

(4) M. Hanack and H. Eggensperger, *Justus Liebigs Ann. Chem.*, **663**, 31 (1963); R. C. Kerber and H. G. Linde, Jr., *J. Org. Chem.*, **31**, 4321 (1966).

(5) Nmr, ^1H (acetone-d_6) δ 6.9 and 5.2, AA′XX′system, 4H, $\frac{1}{2}|J_{AX} + J_{A'X}|$ = 2 Hz, olefinic and bridgehead; 1.7–1.2, 1.0–0.5 (m), cyclopropyl, 8H; ^{13}C (toluene-d_8, ppm) 139.3 (C-5,C-6), 138.5 and 133.3 (C-7 and C-8), 113.3 and 112.8 (CN), 54.7 (C-1, C-4), 47.5 (C-2, C-3) 12.5 (C-9, C-10), 5.6 and 5.3 (C-11, C-12, C-13, and C-14).

(6) M. T. Reetz, R. W. Hoffmann, W. Schäfer, and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **12**, 81 (1973); K. Tori, M. Ueyama, T. Tsuji, H. Matsumura, H. Tanida, H. Iwamura, K. Kushida, T. Nishida, and S. Satoh, *Tetrahedron Lett.*, 327 (1974).

(7) Nmr, ^1H (acetone-d_6, −22°) δ 7.27 (H-5), 6.21 (H-4), 4.96 (H-2), 4.52 (H-3) 1.5–1.0 (H-7, H-8), 0.9–0.4 (H-9, H-10, H-11, H-12); coupling constants (INDOR, ±0.1 Hz), J_{23} = +7.3, J_{34} = +2.9, J_{35} = −1.35, and J_{45} = +5.45 Hz;[8] ^{13}C (acetone-d_6, −20°, ppm) 141.7 (C-6), 139.0 (C-5), 138.5 (C-1), 130.2 (C-4), 112.95, 110.7 and 109.7 (CN), 52.9 and 47.4 (C-2 and C-3), 41.6 and 40.8 (C-13 and C-14), 16.2 and 12.6 (C-7 and C-8), 7.8 and 5.9 × 3 (C-9, C-10, C-11, and C-12); $^1J_{CH}$ (±5 Hz), 165 (C-5), 172 (C-4),[8] 157 and 167 (C-2 and C-3).

(8) P. Laszlo and P. Stang, "Organic Spectroscopy. Principles and Applications," Harper and Row, New York, N.Y., 1971, Chapter 3.

(9) R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, **95**, 5054, 5055 (1973); G. Steiner and R. Huisgen, *ibid.*, **95**, 5056 (1973).

(10) R. Huisgen and G. Steiner, *Tetrahedron Lett.*, 3763 (1973); G. Steiner and R. Huisgen, *ibid.*, 3769 (1973); R. Huisgen, R. Schug, and G. Steiner, *Angew. Chem., Int. Ed. Engl.*, **13**, 80, 81 (1974).

(11) If this were an orbitally concerted step, it would have to be of the 1a, 3s type.

(12) By breaking the 3–14 bond, rather than by opening the 2–13 bond, the latter heterolysis would lead to a less stable cross-conjugated zwitterion, whose only forward reaction—bridgehead olefin formation—is prohibited.

(13) Mp 130–133°; mass spec *m/e* 286 ($M\cdot^+$); (M + 1)/M = 22.45% and (M + 2)/M = 2.31% = in accord with a $C_{18}H_{14}N_4$ formula: nmr, ^1H ($CDCl_3$) δ 6.78 (H-4), 6.31 (H-5), 3.25 (H-3) 1.4–1.0 (H-7, H-8); 0.9–0.4 (H-9, H-10, H-11, H-12), coupling constants[8,14] (INDOR, ±0.1 Hz) J_{45} = +5.45, J_{34} = +1.3, J_{35} = −1.5 Hz; ^{13}C ($CDCl_3$, ppm) 156.8 (C-2), 143.2 (C-4), 134.5 (C-1), 127.4 (C-5), 110.4 and 110.6 (CN), 62.1 and 60.9 (C-13 and C-14), 46.6 (C-6), 36.6 (C-3), 16.2 (C-7, C-8), 3.7 and 3.3 (C-9, C-10, C-11, and C-12).

(14) M. A. Cooper, D. D. Elleman, C. D. Pearce, and S. L. Manatt, *J. Chem. Phys.*, **53**, 2343 (1970); V. A. Korenevsky and N. M. Sergeyev, *J. Amer. Chem. Soc.*, **94**, 8586 (1972).

(15) Whereas nucleophilic attack to assist in the departure of the dicyanomethylene leaving group is blocked in molecule **2** by the steric congestion of C-1, the C-3 position in **3** is left open for interaction in the rear with an ether solvent molecule.

(16) An allowed sigmatropy of the 1s, 5s type, or a dissociation–recombination.

(17) K. N. Houk, L. J. Luskus, and N. S. Bhacca, *J. Amer. Chem. Soc.*, **92**, 6392 (1970); *Tetrahedron Lett.*, 2297 (1972).

(18) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963); S. McLean and P. Haynes, *ibid.*, **21**, 2313 (1965); E. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, **90**, 5284 (1968).

(19) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).

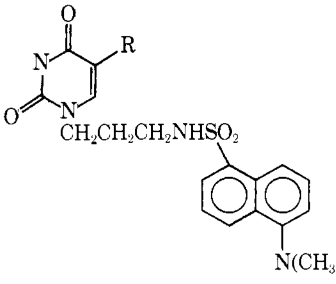
André Cornelis, Pierre Laszlo*
Institut de Chimie, Université de Liège
Sart-Tilman par 4000 Liège, Belgium

Received September 17, 1974

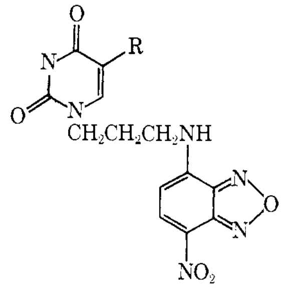
Energy Transfer in Fluorescent Derivatives of Uracil and Thymine

Sir:

We wish to report that light energy (270 nm) absorbed in the uracil or thymine part of the molecules, I–IV, is efficiently transferred to the fluorescent NBD (4-nitrobenzo[2.1.3]oxadiazole) or dansyl (5-dimethylaminonaphthalene-1-sulfonyl) part. The efficiency of transfer is 94% for III, 60% for IV, 38% for I, and 31% for II. The preparation of these compounds is described elsewhere;[1] their identities and purities are confirmed by tlc, pmr, and elementary analysis. Energy transfer was measured (Perkin-Elmer MPF-3 fluorescence spectrometer) by comparison of corrected excitation spectra with absorption spectra (Hitachi 124 spectrometer). Solutions were 3 × 10^{-6} *M* in 20% v/v ethanol-water; Pontachrome Blue Black-R was



I, R = CH_3 (APT-Dansyl)
II, R = H (APU-Dansyl)



III, R = CH_3 (APT-NBD)
IV, R = H (APU-NBD)

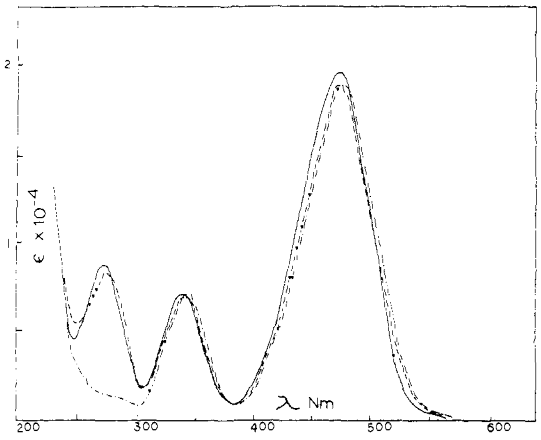


Figure 1. (——) Absorption spectrum of APT-NBD (III), (- - -) corrected excitation spectrum of APT-NBD, (–•–) corrected excitation spectrum of propylamino-NBD. Solvent: 20% (vol) ethanol, fluorescence of NBD at 520 nm was monitored. Slit on excitation and emission side; 2 and 16 nm band width, respectively.

used in the excitation spectra correction. Excitation spectra of mixtures of 3-aminopropylthymine (3-APT) or uracil (3-APU) with propylamino-NBD (or propylaminodansyl) showed no evidence of intermolecular energy transfer at concentrations up to 10^{-3} *M*. A typical spectral comparison is shown in Figure 1.

This transfer of excitation energy from the pyrimidine part to the acceptor part could also be detected chemically. The quantum yield for photohydration of the uracil ring[2]—the only photoreaction for 1-substituted uracils[2]—in APU-NBD (IV) is only 24% of that in 3-APU itself, Table I. This photochemical process is thus efficiently quenched in APU-NBD. Uracil photohydration is not quenched intermolecularly by known singlet or triplet quenchers; the reason for this is considered to be the short lifetime for the reactive excited state.[2]

Comparison of precise absorption spectra of APT, propylamino-NBD, and APT-NBD gives evidence of some hypochromism (2.4% at 270 nm), indicating that the flexibility of the propylamino chain allows some interaction of the two rings in APT-NBD, but the amount of interaction is too small to account for the efficiency of the observed energy transfer by direct contact interaction in a complex (stacking, charge-transfer or other). In the analogous trimethylene-bridged dinucleotide compounds,[1b] a variance in hypochromism (5–10%) was correlated with the rate of photodimerization, but the dimerization quantum yields are very low (about 10^{-3}). We can also add that the efficiency of energy transfer in III was the same in 50% ethylene glycol-water mixtures as it was in 50% ethanol–water mixtures (*i.e.*, no effect of increased viscosity) and that NBD fluorescence in APT-NBD (III) could not be excited by acetone-sensitization (excited acetone is a known triplet donor); thus the excited state of the pyrimidine transferring energy to the NBD part is not a triplet state.

The mechanism of the energy transfer is probably a very weak Förster-type resonance interaction;[3] the separation of the donor and acceptor by the trimethyleneamino chain is 5–10 Å[4] and the overlap of the donor fluorescence spectrum (λ_{max} 330 nm) and the acceptor absorption spectrum (λ_{max} 345 nm) is normal for this type of interaction.

The rate constant for this energy transfer (k_{et}) can then be calculated from the transfer efficiency, with the assumption that constants to be used are those of the reported[5-7] fluorescent state, Table II. The equation used is

$$k_{et} = \phi_{et}\{1/(\phi_f \tau_f)\}$$

Table I. Efficiency of Uracil Photohydration

Compound	Relative rate	Quantum yield
1,3-DMU, water	1.00	$4 \times 10^{-3\,a}$
1,3-DMU, 20% EtOH (v)	0.81	3.23×10^{-4}
1-APU, 20% EtOH(v)	1.31	5.23×10^{-3}
APU-NBD, 20% EtOH (v)	0.31	1.22×10^{-3}

[a] Literature value at DMU = 1×10^{-4}.[2]

Table II. Rate Constants for Energy Transfer

	ϕ_{et}	ϕ_f^0 $(\times 10^4)^{a,b}$	$\tau_{intrinsic}$ (nsec)[a]	k_{et} (M^{-1} sec^{-1})
Uracil (IV)	0.6	1.16	8.3	1.6×10^{12}
Thymine (III)	0.94	1.70	10	1×10^{13}

[a] Reference 5. [b] $\phi_f = (1 - \phi_{et})\phi_f^0$ (ϕ_f^0 donor fluorescence in absence of energy transfer).

where ϕ_{et} = observed efficiency of energy transfer, ϕ_f = donor fluorescence yield, and τ_f = donor intrinsic radiative lifetime. Values of k_{et} thus calculated are shown in Table II. These values can be compared with those calculated by the Forster equation[3a] for the same donor excited state

$$k_{et} = (8.8 \times 10^{-28})(K^2/n^4)(k_{f1})(1/R^6)(\Omega)$$

where Ω is the overlap integral between the donor emission spectrum and the acceptor absorption spectrum. Evaluation of the various quantities in this equation will be described in a later paper. When R is assumed to be 10 Å, $k_{et} = 1.2 \times 10^{11}$; for R = 5 Å, $k_{et} = 7.7 \times 10^{12}$. The value of k_{et} thus observed for the APT-NBD case, for example, can be equaled only by that calculated for a separation which is less than the van der Waals separation of the two groups.

The unusually high values of the rate constants thus calculated for fluorescence energy transfer in III and IV is also found in the rate constant calculated for quenching of uracil photohydration in IV. This rate constant can be calculated from the expression $k_q = \phi_q(k_h/\phi_h)$ where ϕ_h = quantum yield of photohydration in IV, k_h = rate constant for photohydration in APU (5.5×10^9, taken from the known value for uracil photohydration,[5] 2.1×10^8, and the quantum yield of APU photohydrate, Table I), and ϕ_q is taken from the observed quenching of photohydration in IV. The value of k_q thus calculated is 3.4×10^{12}; it will be noted that calculation of k_h also involves the assumption that the state quenched is the fluorescent state. The observation that ϕ_{et} and ϕ_q are very nearly equal suggests that fluorescence sensitization and photohydration quenching involve the same excited state of the donor. The abnormally high values for the energy transfer rate constants calculated from the energy transfer efficiencies suggests that the excited state parameters used in the calculations are inappropriate. Further doubt is cast on these values by Daniels from his observation[5-7] that the peak in the excitation spectra of uracil and thymine is about 10-nm red-shifted from the peak in the absorption spectrum; *i.e.*, the emitting excited state is not the same as that resulting from absorption of light. Daniels suggests[8] that the most likely candidate for the emitting species is an enol of thymine or uracil from excitation of the very low concentration of this enol in aqueous solution (references cited in ref 8). If this is true, then the fluorescence quantum yield must be considerably higher than 10^{-4} and the lifetime correspondingly longer.

Such an enol excited state, however, is not likely to be the precursor to photohydration; 1,3-dimethyluracil, which cannot enolize, photohydrates faster than does uracil, and both 2,4-diethoxyuracil and 4-ethoxy uracil are reported[9] not to form a photohydrate. Finally, although the 270-nm peak in the excitation spectrum of APT-NBD is slightly red shifted from the corresponding peak in the absorption spectrum, the shift is quite small and probably experimental variation. Furthermore, the enol excited state is ruled out as responsible for fluorescence sensitization in our compounds by the high efficiency of such sensitization.

Thus the excited keto form of uracil and thymine is probably the precursor for both photohydration and fluorescence sensitization, and we really have no dependable information about the lifetime of this excited state.

Our data are sufficient, however, to allow us to state that the pyrimidine excited donor state concerned with energy transfer in APU-NBD and APT-NBD, etc., is a singlet excited state, not a "hot ground state" (since singlet excited states of the fluors are produced) and is not a triplet state of the pyrimidine, since NBD fluorescence in APT-NBD could not be sensitized by acetone, a known triplet donor.

Acknowledgment. This work was supported by the National Institutes of Health, Grant GM 19362.

References and Notes

(1) (a) W. A. Summers, Y. J. Lee, and J. G. Burr, *J. Org. Chem.*, in press; (b) see also D. T. Browne, J. Eisinger, and N. J. Leonard, *J. Amer. Chem. Soc.*, **90**, 7302 (1968).

(2) (a) J. G. Burr, E. H. Park, and A. Chan, *J. Amer. Chem. Soc.*, **94**, 5866 (1972); (b) J. G. Burr, *Advan. Photochem.* **6**, 193 (1968); (c) W. A. Summers and J. G. Burr, *J. Phys. Chem.*, **76**, 3137 (1972); (d) W. A. Summers, C. Enwall, and J. G. Burr, *Photochem. Photobiol.*, **17**, 295 (1973), and literature cited in these papers.

(3) (a) T. Förster, "Modern Quantum Chemistry," Part III, O. Sinanoglu, Ed., Academic, New York, N.Y., 1973, p 93; (b) T. Förster, *Discuss. Faraday Soc.*, **27**, 7 (1959); (c) M. Gueron, J. Eisinger, and P. G. Shulman, *J. Chem. Phys.*, **47**, 4077 (1967).

(4) (a) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 2322 (1964); (b) D. E. Breen and R. A. Keller, *ibid.*, **90**, 1935 (1968); (c) R. H. Conrad and L. Brand, *Biochemistry*, **7**, 777 (1968).

(5) W. Hauswirth and M. Daniels, *Chem. Phys. Lett.*, **10**, 140 (1971).

(6) M. Daniels and W. Hauswirth, *Science*, **171**, 675 (1971).

(7) W. Hauswirth and M. Daniels, *Photochem. Photobiol.*, **13**, 157 (1971).

(8) M. Daniels, *Proc. Nat. Acad. Sci. U.S.*, *69*, 2488 (1972).

(9) Unpublished data reported in A. D. McLaren and D. Shugar, "Photochemistry of Proteins and Nucleic Acids," Pergamon Press, Oxford, 1964, p 180. We have confirmed these observations in our own laboratory.

John G. Burr,* W. A. Summers, Y. J. Lee
Department of Chemistry, University of Oklahoma
Norman, Oklahoma 73069

Received July 6, 1974

*Book Reviews**

Aromatic and Heteroaromatic Chemistry. Volume 2. Edited by C. W. BIRD and G. W. H. CHEESEMAN. The Chemical Society, London. *1974. xvi + 519 pp. £16.00.*

This volume of the Specialist Periodical Reports, according to the Editors, is based on the literature reported in Volumes 77 and 78 of *Chemical Abstracts*. The arrangement is as in Volume 1, in 15 chapters with titles largely corresponding to reaction types rather than structure; typical chapter titles are "Condensation Reactions," "Ring Interconversions," "Nucleophilic Substitution." The introductory chapter, "Ring Systems of Topical Interest," is an absorbing account of recent work with unusual or specially significant features. The contributors of the several chapters deserve much appreciation for their valuable efforts in producing a volume of both reference and recent-awareness value.

Raman/IR Atlas. Edited by B. SCHRADER and W. MEIER. Verlag Chemie, Weinheim/Bergstr. 1974. Vol. I: xxxi + ca. 330 pp. DM 230 (sold only in complete set of three volumes, DM 690 by subscription, or DM 795 after appearance of Vol. II).

This work reproduces on each page the infrared and the Raman spectrum of a specific compound, using a common scale linear in wave number. The pages are arranged in an order corresponding to structural features, beginning with saturated hydrocarbons, and eventually reaching organometallics, biopolymers, and inorganic compounds of interest to organic chemists. A prologue in English and German explains the organization, the origin and accuracy of the spectra, and the rationale of the work.

The editors point out that, in the enthusiasm for the successes of infrared spectroscopy in the postwar period, the complementary value of Raman spectra in the study of organic structures has been somewhat overlooked. Whereas infrared spectra give information on asymmetric vibrations of a molecule, Raman spectra complete the picture by responding to symmetrical vibrations. Having the two adjacent to each other thus has the value of giving a reasonably complete picture of the "mechanical" vibrations of a molecule.

This work is in loose-leaf form, and will comprise three deliveries to fill altogether two volumes with spectra of about 1000 selected compounds.

Saturated Heterocyclic Chemistry. Volume 2. Edited by W. PARKER (University of Stirling). The Chemical Society, London. *1974. 407 pp. £13.50.*

This volume in the series Specialist Periodical Reports covers the calendar year 1972. It is arranged according to ring size, with a final chapter on bridged systems. Within the chapters, the material is grouped under the headings Physical Methods, Formation, and Reactions. The aim has been to review the developments of the year with a limited amount of selectivity. The large amount of material covered can be appreciated from the fact that the chapter on three-membered rings alone contains 423 references. The chapter entitled "Medium-sized Rings" also contains a section on macrocycles, in which crown ethers and related amines are discussed. There is an author index.

Statistical Thermodynamics. By DONALD A. MCQUARRIE (Indiana University). Harper and Row Publishers, New York, N.Y. 1973. xi + 343 pp. $14.95.

This book is the first fifteen chapters of a larger work on statistical mechanics scheduled for publication this year. The author states that the book is designed as a text for a first-year graduate course; for this, it is well suited.

The material covered in this book may be divided conveniently into three parts. The first part, comprising one chapter (1) of 34 pages, consists of a very brief exposition of classical and quantum mechanics and a discussion of some mathematical concepts (such as Legendre transformations) not generally covered in an undergraduate course in thermodynamics. The second part consists of four chapters (2, 3, 4, and 7) of 62 pages and deals with the fundamental definitions and postulates of statistical mechanics. The third part (ten chapters, 232 pages) attempts to show the power of statistical thermodynamics by treating a variety of topics dealing with gases (ideal monatomic, ideal diatomic, ideal polyatomic, and imperfect), crystals, liquids, and polymers.

The author, a student of T. L. Hill, states that his approach is similar to that found in the latter's "An Introduction to Statistical Thermodynamics." In general, the principal difference between these two books is one of scope and, at times, depth of coverage. Despite a somewhat narrower scope and despite its obvious paral-

---

* Unsigned book reviews are by the Book Review Editor.