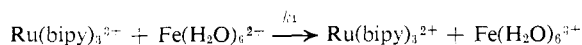


Both paraquat and *trans*-4,4'-BPE²⁺ are relatively weak oxidants (Table I). Since their rates of electron transfer quenching of Ru(bipy)₃^{2+*} are probably diffusion controlled, the net redox reactions involved, Ru(bipy)₃^{2+*} + ox → Ru(bipy)₃³⁺ + red, must be favored thermodynamically. If Δ*G* ≤ 0, an upper limit for the reduction potential for the excited state couple, Ru(bipy)₃³⁺ + e → Ru(bipy)₃^{2+*}, can be estimated as *E* ≤ -0.49 V in acetonitrile *vs.* the saturated sodium chloride calomel electrode.

Aqueous deaerated solutions of Ru(bipy)₃²⁺ at room temperature were flashed in the presence of Fe(H₂O)₆³⁺ (in 1.0 *M* HClO₄) and in the presence of Ru(NH₃)₆³⁺ (in 1.0 *M* CF₃COOH). In both cases, a very rapid initial bleaching was followed by slower but complete regeneration of the Ru(bipy)₃²⁺ absorbance at 450 nm (see Scheme I). The reaction between Ru(bipy)₃^{2+*} and Fe(H₂O)₆³⁺ clearly involves *net* electron transfer quenching (see below), but the intimate details of the quenching process are not certain. Direct photolysis of acidic solutions of Fe(H₂O)₆³⁺ with 254-nm light is known to give hydroxy radicals.¹⁵ The excited state energy of Ru(bipy)₃^{2+*} is apparently sufficient to sensitize the production of hydroxy radicals.¹⁶ In principle, the appearance of Ru(bipy)₃³⁺ could be accounted for by a secondary redox reaction between Ru(bipy)₃²⁺ and OH formed in the Ru(bipy)₃²⁺ sensitized oxidation of water by Fe³⁺(aq). However, this mechanism can be ruled out. Flash photolysis studies (Ru(bipy)₃²⁺ = 2.0 × 10⁻⁵ *M*; Fe(H₂O)₆³⁺ = 1.5 × 10⁻³ *M*) were carried out in the presence of relatively high concentrations of the known OH scavengers Fe(H₂O)₆²⁺ (6 × 10⁻³ to 4 × 10⁻⁴ *M*) and isopropyl alcohol (up to 60% by volume). In all cases, the initial yield of Ru(bipy)₃³⁺ remained essentially the same even under conditions where complete scavenging of hydroxy radicals would have occurred. It thus seems likely that quenching of Ru(bipy)₃^{2+*} by Fe(H₂O)₆³⁺ occurs by direct electron transfer (reaction 2).

When taken together the series of reactions given in Scheme I constitute a flash photolysis relaxation technique for measuring the rates of very rapid electron transfer reactions. Under conditions where the quenching step is made rapid, the dark reaction (eq 3) involving back-electron transfer between the ground state ions becomes rate determining. Under conditions where electron transfer is the slow step, the rate of regeneration of Ru(bipy)₃²⁺ by Fe(H₂O)₆²⁺ was shown to be first order in Fe(H₂O)₆²⁺ and in Ru(bipy)₃³⁺ and independent of Fe(H₂O)₆³⁺ indicating that the regeneration reaction is



The calculated second-order rate constant, *k*₁ = 1.0 × 10⁶ *M*⁻¹ sec⁻¹, is in good agreement with the value found by Braddock and Meyer¹⁷ at 25°, *k* = 6.41 ± 0.38 × 10⁵ *M*⁻¹ sec⁻¹, by stopped-flow techniques. The rates of regeneration of Ru(bipy)₃²⁺ in solutions initially containing Ru(NH₃)₆³⁺, paraquat, and *trans*-4,4'-BPE²⁺ were also studied (Table II). In all three

(15) G. Adamson, D. L. Baulch, and F. S. Dainton, *Trans. Faraday Soc.*, **58**, 1388 (1962).

(16) Fe³⁺(aq) + H₂O → Fe²⁺(aq) + OH + H⁺ in 1.0 *M* acid, Δ*G*^o = 46 kcal/mol.

(17) J. N. Braddock and T. J. Meyer, *J. Amer. Chem. Soc.*, **95**, 3158 (1973).

Table II. Rate and Equilibrium Constant Data for Electron Transfer Reactions Involving Ru(bipy)₃³⁺

Reaction	<i>k</i> , <i>M</i> ⁻¹ sec ⁻¹	<i>K</i>
Ru(bipy) ₃ ^{2+*} + Fe(H ₂ O) ₆ ²⁺ → Ru(bipy) ₃ ²⁺ + Fe(H ₂ O) ₆ ³⁺	1.0 × 10 ^{6a}	6.1 × 10 ^{8a}
Ru(bipy) ₃ ^{2+*} + Ru(NH ₃) ₆ ²⁺ → Ru(bipy) ₃ ²⁺ + Ru(NH ₃) ₆ ³⁺	3.68 ± 0.60 × 10 ^{9b}	1.9 × 10 ^{20a}
Ru(bipy) ₃ ^{2+*} + paraquat ⁺ → Ru(bipy) ₃ ²⁺ + paraquat ²⁻	(8.3 ± 1.6) × 10 ^{9c}	2.5 × 10 ^{29c}
Ru(bipy) ₃ ^{2+*} + <i>trans</i> -4,4'-BPE ⁺ → Ru(bipy) ₃ ²⁺ + <i>trans</i> -4,4'-BPE ²⁺	~5 × 10 ^{9c}	1.2 × 10 ^{30c}

^a In 1.0 *M* aqueous HClO₄ at room temperature. ^b In 1.0 *M* aqueous CF₃CO₂H at room temperature. ^c In acetonitrile containing 0.1 *M* tetra-*N*-ethylammonium perchlorate at room temperature.

cases the rate of appearance of Ru(bipy)₃²⁺ follows second-order (equal concentration) kinetics indicating that the dark electron transfer reaction (eq 3) was being studied.

As indicated by the rate and equilibrium constant data in Table II, the flash photolysis relaxation technique is remarkable in that reactions which are highly favored thermodynamically can be measured.¹⁸

(18) Support of this work by the Army Research Office (Grant No. DA-ARO-D-31-124-G1097) and the National Institutes of Health (Grant No. GM 15,238) is gratefully acknowledged.

C. R. Bock, T. J. Meyer,* D. G. Whitten*

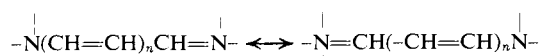
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Received March 12, 1974

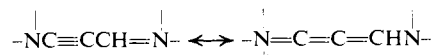
A New Resonance System. Ethnological Amidinium Compounds. Acetylenic Analogs of Cyanine Dyes

Sir:

Numerous examples of compounds that contain the amidinium resonance system are known. We should



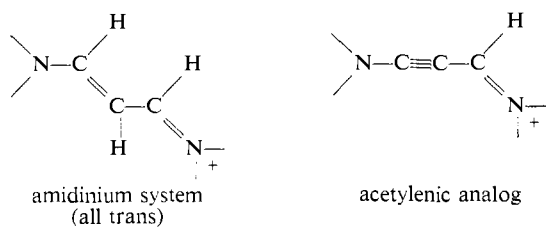
like to report the first synthesis of analogs that contain a triple bond as part of the conjugated chain. The simplest such resonance system may be represented as follows.



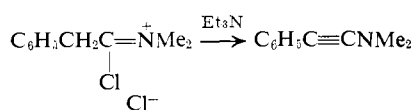
Compounds containing such a functionality could be considered to be the oxidation products of the corresponding amidinium compound, in which two hydrogen atoms have been replaced by a pair of electrons in a π-orbital orthogonal to that of the conjugated chain. Such a transformation would have important electronic and steric implications. In contrast to amidinium compounds, the extreme structures representative of such a resonance system cannot be identical. The resulting asymmetric electronic distribution might be expected to produce a hypsochromic shift in electronic absorption relative to that of the corresponding amidinium compound, since progressive increase in electronic asymmetry in the amidinium system produces cor-

respondingly increasing hypsochromic displacement of the absorption maximum, as is evidenced by Brooker's extensive investigations in the field of cyanine dyes.¹

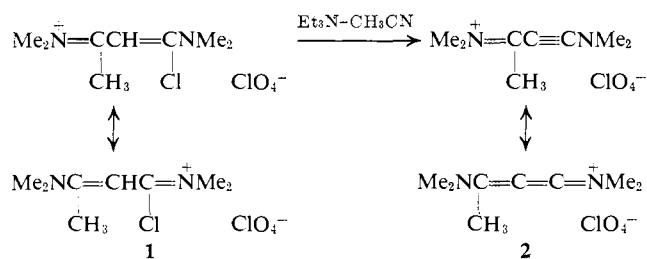
A second contrast between the two resonance systems is apparent when their respective stereochemical requirements are considered, since the inclusion of a triple bond in the conjugated chain requires colinearity of four consecutive atoms.



Ynamines have been obtained by elimination of hydrogen chloride from α -halogenoiminium salts.² For example



We have found that corresponding elimination of hydrogen chloride from **1** gives the acetylenic amidinium analog, **2**. Compound **1** was obtained by the self-



condensation reaction of the Vilsmeier complex of dimethylacetamide and phosphoryl chloride.³

Structure **2** was assigned on the basis of uv [λ_{max} (CH₃CN) 309 nm], ir (KBr) (very strong band at 2180 cm⁻¹), and nmr spectra and elemental analysis.

Similar considerations to those discussed above apply to a special class of vinylogous amidinium salts, the cyanine dyes. Cyanines are of great importance as sensitizers in photography. Their sensitizing properties are greatly influenced by both their light-absorption characteristics and their stereochemistry.⁴ Thus, the effect of introduction of a triple bond into the conjugated chain of a cyanine on the dye's electronic and steric⁵ properties, and thus on its behavior as a photographic sensitizer, is of considerable interest.

(1) L. G. S. Brooker, A. L. Sklar, H. W. J. Cressman, G. H. Keyes, L. A. Smith, R. H. Sprague, E. Van Lare, G. Van Zandt, F. L. White, and W. W. Williams, *J. Amer. Chem. Soc.*, **67**, 1875 (1945), and references therein.

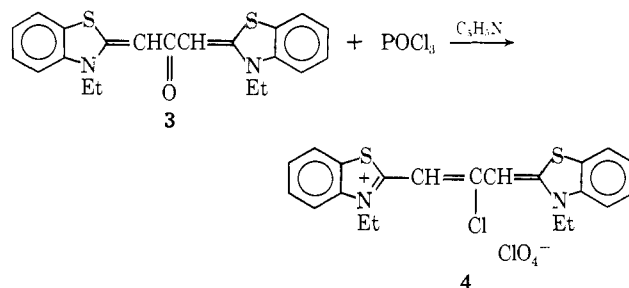
(2) H. G. Viehe in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 12.

(3) This reaction was studied by H. Bredereck, R. Gompper, and K. Klemm, *Chem. Ber.*, **92**, 1456 (1959), but only the hydrolysis products of **1** were isolated.

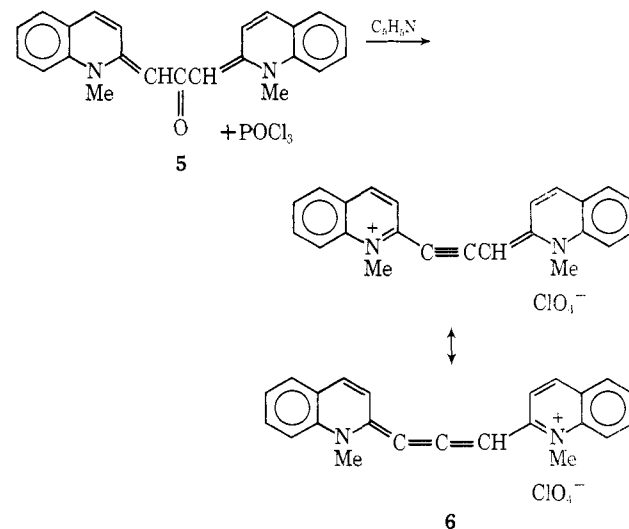
(4) For excellent reviews of this subject see (a) H. Meier, "Spectral Sensitization," The Focal Press, New York, N. Y., 1968, Chapter 2; (b) L. G. S. Brooker in "The Theory of the Photographic Process," 3rd ed, T. H. James, Ed., Macmillan, New York, N. Y., 1966, Chapter 11.

(5) An X-ray analysis of **9** has been carried out. D. L. Smith, to be submitted for publication in *Acta Crystallogr.*

Treatment of the ketone **3**⁶ with phosphoryl chloride in pyridine solution at room temperature gave the meso-chloro carbocyanine **4**, which was conveniently isolated as its perchlorate salt.



Under the same conditions, the ketone **5** did not give the expected analog of **4**. Instead, elimination of hydrogen chloride occurred with the formation of the acetylenic cyanine analog^{7,8} **6**.



When the above reaction was applied to a number of ketones related to **3** and **5**, it became apparent that, under the above conditions, elimination of hydrogen chloride to yield an acetylenic dye occurred only when the planar configuration of the meso-chloro carbocyanine was seriously crowded.⁹ Thus dyes **6-9** were obtained directly. Dehydrochlorination of uncrowded dyes such as **4** can be brought about, however, by warming in 50% aqueous acetonitrile containing a small excess of triethylamine.

Comparison of the visible absorption maxima of five acetylenic dyes with those of the corresponding carbocyanines, as shown in Table I, reflects the hypsochromic shift anticipated for introduction of a triple bond into the conjugated system. In general, the molar extinction coefficients of the acetylenic dyes are about two-thirds of those for the corresponding carbocyanines.

As is the case with ynamines,² compounds containing acidic hydrogen atoms, such as hydrogen chloride or bromide, add across the triple bond of these dyes to

(6) L. G. S. Brooker and F. L. White, U. S. Patent 2,520,358 (1950).

(7) Cyanines are members of a broader class of dyes, the polymethines. We suggest the term "methyne" as generic for dyes that may be considered to be derived from the polymethines by replacement of one or more of the double bonds in the conjugated chain of the dye by a triple bond.

(8) Previous attempts to prepare dyes of this class were unsuccessful. P. Collet, Thesis, Conservatoire National des Arts et Métiers, 1964.

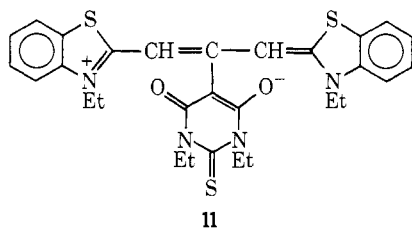
(9) This crowding is clearly indicated by molecular models.

Table I. Visible Absorption Maxima of $R_1^+C\equiv CCH=R_2 ClO_4^-$

Dye	R_1	R_2	λ_{max} (CH_3CN), ^a nm	$\epsilon_{max}^a \times 10^{-4}$
6			568 (601)	8.8 (15.2)
7			539 (581)	21.2 (31.8)
8			513 (541)	8.3 (15.2)
9			473 (513)	14.0 (21.0)
10			513 (553)	9.9 (15.7)

^a The value for the corresponding carbocyanine is shown in parentheses.

give meso-substituted carbocyanines. Addition of weaker acids such as aryl thiols is catalyzed by base. The addition of 1,3-diethyl-2-thiobarbituric acid to give dyes such as **11** exemplifies a general route for the preparation of allolopolar cyanines.^{4b}



Further studies of this interesting new class of compounds are in progress.

John D. Mee

Research Laboratories, Eastman Kodak Company
Rochester, New York 14650

Received January 25, 1974

Tricyclo[3.1.1.0^{3,6}]heptane-6-carboxylic Acid¹

Sir:

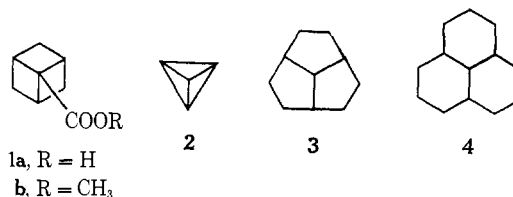
We wish to report the synthesis of tricyclo[3.1.1.0^{3,6}]heptane-6-carboxylic acid (**1**), the first known example of this ring system in which the three alternate carbon atoms of a cyclohexane ring are bonded to a single bridging carbon unit. Other members of this general family of molecules involving the symmetrical bridging of a ring perimeter by a single carbon atom include the elusive tetrahedrane² (**2**) and the well-documented triquinacene³ (**3**) and phenalene⁴ (**4**) systems. Al-

(1) Financial support of this research by the Robert A. Welch Foundation is gratefully acknowledged.

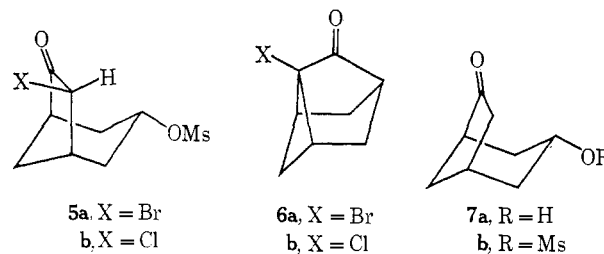
(2) P. B. Shevlin and A. P. Wolff, *J. Amer. Chem. Soc.*, **92**, 406 (1970).

(3) (a) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, **86**, 3162, (1964); (b) R. Russo, Y. Lambert, and P. Deslongchamps, *Can. J. Chem.*, **49**, 531 (1971).

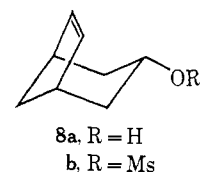
(4) (a) H. C. Brown and W. C. Dickinson, *J. Amer. Chem. Soc.*, **91**, 1226 (1969); (b) H. C. Brown and E. Negishi, *ibid.*, **89**, 5478 (1967).



ternatively, acid **1** can be envisioned as a trisnoradamantane derivative. Our synthetic approach involved formation of the first four-membered ring of acid **1** by intramolecular ring closure⁵ of 7-halobicyclo[3.2.1]octanone **5** to give the 6-halotricyclo[3.2.1.0^{3,6}]octanone intermediate **6**. The two remaining four-membered rings were generated by a base induced semibenzilic acid ring contraction of **6** to yield acid **1**.



The previously reported^{5,6} *exo*-bicyclo[3.2.1]octan-3-ol-6-one (**7a**) was converted⁷ into the crystalline *exo*-mesylate **7b** (70%)⁸ and then into a *single* 7-bromo derivative **5a** (mp 77.5–79.2°, 96%)^{8,9} by treatment with bromine in $CHCl_3$. Alternatively, a *single* 7-chlorobicyclo[3.2.1]octanone **5b** (mp 75.8–79.5°)^{8,10} was obtained in 84% yield by chromyl chloride¹¹ oxidation of *exo*-bicyclo[3.2.1]oct-5-en-3-yl mesylate (**8a**)⁸ which was prepared from the known¹² alcohol **8b** (88%). The



halogen atom in both bicyclo ketones, **5**, is assigned as *exo* on the basis of the observed coupling constant for the C-7 proton ($J = 2-3$ Hz).^{13,14} Treatment of the bicyclic halo ketones, **5**, with sodium hexamethyldisilazane¹⁵ (benzene, 70°, 10 min) furnished the cor-

(5) S. A. Monti and S.-S. Yuan, *Tetrahedron Lett.*, 3627 (1969).

(6) This procedure⁸ yields **7a** of ca. 70% isomeric purity: J. M. Harless, unpublished observations.

(7) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

(8) All new compounds gave satisfactory spectral and combustion analysis data.

(9) Spectral data for **5a**: ir ($CHCl_3$) 1755 (C=O); 1362, 1338, and 1182 cm^{-1} (OSO_2CH_3); nmr ($CDCl_3$) δ 1.85–2.90 (m, 8), 3.10 (s, 3, $-CH_3$), 4.53 (d, 1, *endo* C-H, $J = 2-3$ Hz), 4.78 ppm (sept, 1, *exo* C-H, $J = 11, 6$ Hz).

(10) Spectra. data for **5b**: ir ($CHCl_3$) 1758 (C=O); 1360, 1340, and 1180 cm^{-1} (OSO_2CH_3); nmr ($CDCl_3$) δ 1.57–2.90 (m, 8), 3.00 (s, 3, $-CH_3$), 4.07 (d, 1, *endo* C-H, $J = 2-3$ Hz), 4.70 ppm (sept, 1, *endo* C-H, $J = 12, 6$ Hz).

(11) K. B. Sharpless and A. Y. Teranishi, *J. Org. Chem.*, **38**, 185 (1973).

(12) N. A. LeBel and R. J. Maxwell, *J. Amer. Chem. Soc.*, **91**, 2307 (1969).

(13) Pyrrolidine catalyzed isomerization of **5b** yielded the *endo* 7-chloro derivative, δ 4.33 ppm (d, 1, *exo* C-H, $J = 6$ Hz).

(14) For a study on the stereoselectivity of chromyl chloride oxidations, see F. W. Bachelor and U. O. Cherigan, *Tetrahedron Lett.*, 3291 (1973).

(15) U. Wannagat and H. Niederprüm, *Chem. Ber.*, **94**, 1540 (1961).