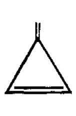
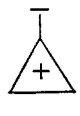
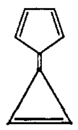
Triapentafulvalene-3,6-quinone Derivatives. Triafulvenes with a "Low" Dipole Moment[1]

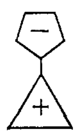
Sir:

In the studies of triafulvene and triapentafulvalene derivatives (**1**, **2**) carried out so far, it has been assumed implicitly that dipolar structures (**1a**, **2a**) contribute significantly to the ground state and thus cause a substantial degree of aromaticity of the molecules.[2] Thus, it is characteristic that most compounds of these series possess electron-withdrawing groups at the exocyclic carbon atom of **1** or in the five-membered ring of **2**, that the moments of the substituents have the same direction as the moment of the triafulvene system, and that their dipole moments are unusually high (>5 D). We wish to report two stable "triapentafulvalene-3,6-quinone" derivatives in which the dipole moments of the functional (carbonyl) groups have a direction opposite to the moment of the triafulvene system.


1


1a

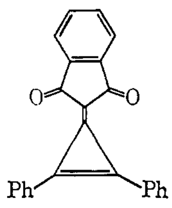

2


2a

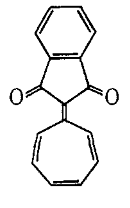
Condensation of 3,3-dichloro-1,2-diphenylcyclopropene[3] with indan-1,3-dione at 130° afforded a 50% yield of 1,2-diphenyl-4,5-benzotriapentafulvalene-3,6-quinone (**3**) as yellow plates, mp 228° (from benzene). *Anal.* Calcd for $C_{24}H_{14}O_2$: C, 86.2; H, 4.2; mol wt, 334. Found: C, 86.3; H, 4.4; mol wt, 334 (mass spectroscopy). Among the infrared frequencies outstanding are those at 1837 cm^{-1} (1,2-disubstituted triafulvenes)[4] and 1660 cm^{-1} (C=O) (in CH_2Cl_2);[5] $\lambda_{\max}^{CH_3CN}$ mμ (log ε) 231 (4.76), 266 s (4.46), 280 (4.12), 296 (4.36), and 342 (4.74). The 342-mμ peak remains practically the same in benzene, carbon tetrachloride, cyclohexane, chloroform, dioxane, diethyl ether, and ethanol, indicating no change in moment in the transition from the ground to the excited state.[6]

If one accepts the view[1] that dipolar forms such as **1a** and **2a** confer on the molecules an aromatic character ($4n + 2$ rule) and if one recalls the expected similarity between the triafulvene and the heptafulvene systems, then the more pronounced aromatic character of **3** expresses itself best in the magnitude of the dipole moment (3.66 ± 0.03 D, benzene, 30°) if compared with that of 2-benzylideneindan-1,3-dione (1.2 ± 0.1 D, benzene, 30°) and that of the analogous 2,3-benzopentaheptafulvalene-1,4-quinone (**4**) (2.48 D).[7] The comparison of these moments further shows that in accordance with the tendency of the three- and the seven-membered ring in **3** and **4** to carry negative charges, the resultant moment in these molecules (contrary to the benzylidene derivative) is directed toward the five-membered ring. The effect is larger by 1.2 D in **3** than in **4**. As **3** is stable to oxidation and high temperature and does not tend to stabilization by rearrangement in spite of its relatively low moment, it is clear that stabilization of the triafulvene system (**1**) can be achieved by electron-withdrawing substituents even if the moment resulting from them is directed *toward* the three-membered ring.

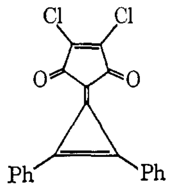
Direct evidence concerning the orientation of the carbonyl groups of **3** comes from its nmr spectrum: δ^{CDCl_3} (Varian HA-100) 8.80–8.65 (m, 4 H *ortho* in the phenyl groups), 7.86–7.72 (m, 2 H *ortho* to the C=O of the indandione moiety), and 7.72–7.50 (m, remaining 8 H) ppm. The difference *ortho* − (*meta* + *para*) (1.1 ppm) is much larger than that usually observed for the phenyl rings in the 1,2-diphenyltriafulvenes and cyclopropenium salts and ascribed to the positive charge in the three-membered ring.[8–10] We submit that in the case of **3** this effect is of minor importance. The main cause for the strong deshielding of the *ortho* hydrogen atoms is the diamagnetic anisotropy of the carbonyl groups: they are directed *toward* the cyclopropene ring so that the distance between the *ortho* hydrogen atoms and the *nearest* oxygen atom is small.[11]



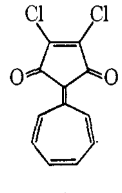
3



4



5



6

Condensation of 3,3-dichloro-1,2-diphenylcyclopropene with 1,2-dichlorocyclopent-1-ene-3,5-dione[12] gave, in 37% yield, 4,5-dichloro-1,2-diphenyltriapentafulvalene-3,6-quinone (**5**) as bright yellow needles, mp 282° (from benzene). *Anal.* Calcd for $C_{20}H_{10}Cl_2O_2$: C, 68.0; H, 2.8; Cl, 20.1; mol wt, 353. Found: C, 68.1; H, 3.1; Cl, 20.5; mol wt, 353 (mass spectroscopy). The infrared spectrum (in CH_2Cl_2) shows the triafulvene frequency at 1847 cm^{-1} while the carbonyl absorption appears at 1695 and 1669 cm^{-1}; $\lambda_{\max}^{CH_3CN}$ mμ (log ε) 241 (4.46), 249 (4.47), 305 s (4.54), 316 (4.65), and 344 s (4.18). Here, too, the wavelength of the longest absorption band is independent of the solvent. The dipole moment (6.11 ± 0.03 D, benzene, 30°) is again larger (by 1.2 D) than that of 2,3-dichloropentaheptafulvalene-1,4-quinone (**6**).[7]

Thus, comparing **3** and **5** with **4** and **6** one finds that the cyclopropenylidenecyclopentadienide structure is more favored than the cycloheptatrienylidenecyclo-

---

[1] Fulvenes and Thermochromic Ethylenes. XLIX. For part XLVIII see C. Lifshitz, E. D. Bergmann, M. Rabinovitz, and I. Agranat, *J. Chem. Soc.*, in press.

[2] A. S. Kende, *Trans. N. Y. Acad. Sci.*, **28**, 981 (1966).

[3] *Cf.* S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 4215 (1964); B. Foehlisch and P. Buergle, *Ann.*, 701, 67 (1967).

[4] I. Agranat and E. D. Bergmann, *Tetrahedron Letters*, 2373 (1966).

[5] For comparison, for 2-benzylidene-1,3-indan-1,3-dione the carbonyl frequencies appear at 1734 and 1691 cm^{-1}.

[6] For the similar behavior of 3,4,5,6-tetrachloro-1,2-diphenyltriapentafulvalene see E. D. Bergmann and I. Agranat, *Tetrahedron*, **22**, 1275 (1966).

[7] S. Katagiri, I. Murata, Y. Kitahara, and H. Azumi, *Bull. Chem. Soc. Japan*, **38**, 281 (1965).

[8] R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962).

[9] S. Andreades, *ibid.*, **87**, 3941 (1965).

[10] T. Eicher and A. Loeschner, *Z. Naturforsch.*, **21b**, 899 (1966).

[11] The same holds true in the case of 1-(2,3-diphenylcyclopropenylidene)-4,4-dimethylcyclohexane-2,6-dione for which the analogous difference is 1.00 ppm. Thus, the argument put forward by Eicher and Loeschner[10] that the effect is entirely due to the positive charge in the three-membered ring appears unwarranted.

[12] A. Roedig and L. Hoernig, *Chem. Ber.*, **88**, 2003 (1955).

pentadienide structure in spite of the greater strain in the former.

Israel Agranat, Ruth M. J. Loewenstein, Ernst D. Bergmann
Department of Organic Chemistry
The Hebrew University of Jerusalem, Jerusalem, Israel
Received November 27, 1967

Bifunctional Catalysis of the Dedeuteration of Isobutyraldehyde-2-*d* by Polyethylenimines[1]

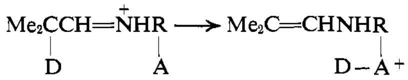
Sir:

Previous work showed that with moderate concentrations of a primary amine salt and a buffer the dedeuteration of isobutyraldehyde-2-*d* is largely a third-order reaction, first order in aldehyde, first order in buffer base, and first order in amine salt.[1b,2-4] This reaction is believed to involve the reversible transformation of deuterioaldehyde to the corresponding N-alkyliminium ion followed by removal of deuterium by the buffer base (B).

$$\mathrm{Me_2CDCHO + RNH_3^+ \rightleftharpoons Me_2CDCH{=}NHR^+ + H_2O}$$

$$\mathrm{Me_2CDCH{=}NHR^+ + B \longrightarrow Me_2C{=}CHNHR + BD^+}$$

We have now found that poly(ethylenimine)s are relatively effective catalysts for this reaction, and we suggest that they are acting as bifunctional catalysts. Apparently the aldehyde reacts with the catalyst to give imines (and imidazolidines and probably other complexes), which are in equilibrium with the corresponding iminium ions. The deuterium atoms in such iminium ions may then be removed by other amino groups in the poly(ethyleneimine) residue; that is, the rate-controlling step of the reaction is of the form



$$\underset{\mathrm{D}}{\mathrm{Me_2C}}\mathrm{H{=}}\underset{\mathrm{A}}{\overset{+}{\mathrm{N}}}\mathrm{HR} \longrightarrow \mathrm{Me_2C{=}CHNHR} \quad \mathrm{D{-}A^+}$$

where A is the amino group that removes the deuterium.

The kinetics of the dedeuteration of 0.053 *M* isobutyraldehyde at pH 8.5 were studied in the presence of poly(ethylenimine)s (PEI's)[5,6] and related simpler compounds. First-order rate constants (k_p), obtained as described previously,[1b,2-4] using about 0.1 *N*[7] catalysts, are listed in Table I. Even N,N-dimethylethylenediamine, the most effective of the methylated ethylenediamines (probably because it is the only one that cannot tie up the aldehyde as an imidazolidine), is less than one-fourth as good a catalyst as the larger PEI's. A fundamental difference in catalysis by the ethylenediamines and the PEI's is shown by the plot of k_p and absorbance at the aldehyde maximum *vs.* catalyst concentration in Figure 1. With N,N-dimethylethylenediamine (and also ethylenediamine and N-methylethylenediamine, whose behavior is qualitatively similar), two catalyst molecules perform important functions. One transforms the aldehyde to imine and then to iminium ion;[8] the second removes the deuterium. Therefore the rate of dedeuteration continues to increase with increasing N,N-dimethylethylenediamine concentration, even at concentrations (above ~0.7 *N*) where there is no longer a major increase in the amount of aldehyde that is present as imine. With PEI-1800, on the other hand, when the concentration of catalyst exceeds that required to complex almost all the aldehyde, addition of more catalyst no longer increases the reaction rate significantly. It therefore appears that

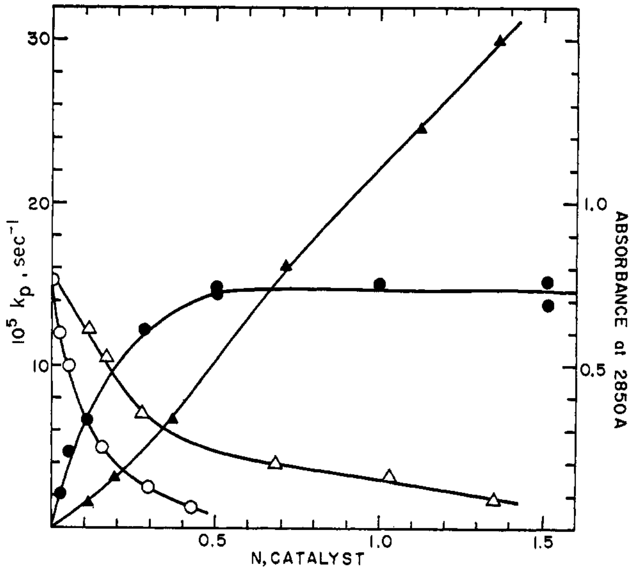


Figure 1. Dedeuteration of 0.053 *M* isobutyraldehyde-2-*d* at 35° and pH 8.4 ± 0.2: ●, k_p in the presence of PEI-1800; ▲, k_p in the presence of $\mathrm{Me_2NCH_2CH_2NH_2}$; ○, absorbance in the presence of PEI-1800; △, absorbance in the presence of $\mathrm{Me_2NCH_2CH_2NH_2}$.

Table I. First-Order Rate Constants for the Dedeuteration of 0.053 *M* Isobutyraldehyde-2-*d* at 35° and pH 8.50 ± 0.05

Catalyst (*N*)	$10^5 k_p$ (sec^{-1})
Ethylenediamine (0.101)	0.20
N-Methylethylenediamine (0.097)	0.30
N,N′-Dimethylethylenediamine (0.099)	0.36
N,N-Dimethylethylenediamine (0.099)	1.5
Diethylenetriamine (0.099)	0.90
PEI-146[a] (0.100)	2.0
PEI-190[a] (0.100)	3.0
PEI-600 (0.107)	7.5
PEI-1200 (0.115)	7.9
PEI-1800 (0.104)	6.6
PEI-60,000 (0.101)	6.2

[a] PEI-146 and PEI-190 are materials labeled triethylenetetramine and tetraethylenepentamine, respectively, but they are technical grade chemicals and are listed as PEI's here since, like the higher polymers, each is a mixture of a number of different compounds.

---

[1] (a) This investigation was supported in part by Public Health Service Research Grant AM 10378 from the National Institute of Arthritis and Metabolic Diseases. (b) Catalysis of α-Hydrogen Exchange. VIII. For part VII see J. Hine, B. C. Menon, J. Mulders, and J. P. Idoux, *J. Org. Chem.*, **32**, 3850 (1967).

[2] J. Hine, B. C. Menon, J. H. Jensen, and J. Mulders, *J. Am. Chem. Soc.*, **88**, 3367 (1966).

[3] J. Hine, F. C. Kokesh, K. G. Hampton, and J. Mulders, *ibid.*, **89**, 1205 (1967).

[4] J. Hine, J. Mulders, J. G. Houston, and J. P. Idoux, *J. Org. Chem.*, **32**, 2205 (1967).

[5] Hydrochloric acid was added to adjust the pH.

[6] PEI-X is a poly(ethylenimine) with a number-average molecular weight of *X*. The polymers used, obtained from the Dow Chemical Co., are sometimes written as $(\mathrm{-CH_2CH_2NH-})_n$ but are said to be acyclic and to have a degree of branching such that the ratio of primary to secondary to tertiary amino groups is about 1:2:1.

[7] Concentrations refer to the number of equivalents of amino groups.

[8] For several reasons the iminium ion would be expected to be almost entirely *trans*. This is one reason why bifunctional catalysis does not become important until there are rather widely separated amino groups in the catalyst.