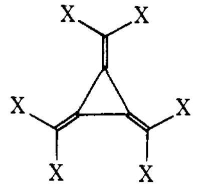
Negatively Substituted Trimethylenecyclopropane Dianions

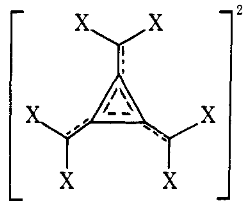
Sir:

Trimethylenecyclopropane (TMCP),[1] **1** (X = H), is isomeric with benzene, but has three essentially localized single and double bonds. Because of its D_{3h} symmetry, the LUMO is nondegenerate and symmetric with respect to the C_3 axis, and has a node between the ring and radial carbon atoms. Thus, in the TMCP dianion having this MO now occupied, both the ring and radial bonds are expected to have substantial π bond orders, and it becomes of particular interest if the MO in question can be sufficiently stabilized below the nonbonding level. Perturbation calculations suggest that this may be achieved simply by making the radial carbon atoms more electronegative.[2-4]



$[C_6X_6]^0$

1

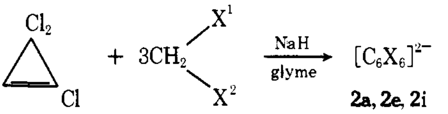


$[C_6X_6]^{2-}$

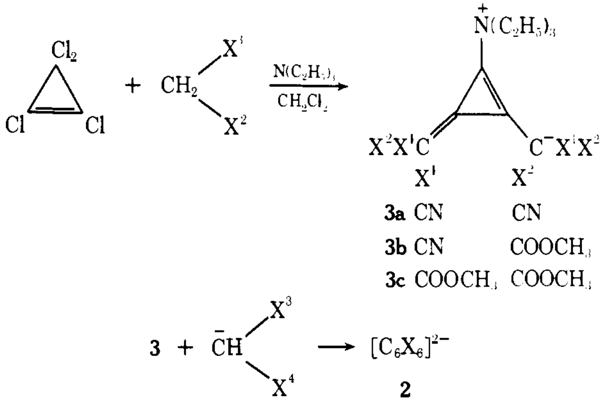
2

In this communication we wish to report the synthesis and properties of the TMCP dianions **2** substituted fully with cyano and/or ester groups.[5]

Hexacyanotrimethylenecyclopropanediide (**2a**) was obtained by the reaction of tetrachlorocyclopropene, C_3Cl_4, with 3 equiv of malononitrile in glyme in the presence of 6 equiv of sodium hydride, and isolated as the bis(tetrabutylammonium) (TBA) salt,[6] mp 210-211 °C. The formation of **2a** in almost quantitative yield reflects its high stability and contrasts markedly to the exclusive ring opening in the reaction of C_3Cl_4 with alcohol and water.[7] Similarly, the reaction of C_3Cl_4 with methyl cyanoacetate and dimethyl malonate afforded[8] the dianions, **2e** and **2i** (see Table I), respectively.



When the reactions were performed in dichloromethane using triethylamine as a base, the zwitterionic methylenecyclopropenes, **3**, were obtained as colorless solids in 50-86% yields. The triethylamino group of **3** could further be replaced by another active methylene compound. This second step can be carried out by adding a solution of **3** in HMPA into either a solution or a suspension of the sodio derivative of an appropriate active methylene compound[9] in methanol, glyme, or DMSO. By these procedures dianions, **2**, with a different assortment and location of the substituents were prepared and are summarized in Table I.

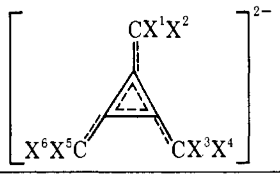


While **2a** was a very weak base and could not be protonated in acetic acid or dilute hydrochloric acid, the dianions became stronger bases as the number of ester groups increased. Thus, **2g** and **2h** were monoprotonated and **2i** was diprotonated by dilute acid. In these cases, it was more convenient to isolate the monohydrogen TBA salts or the conjugate diacid. The protonated species could be cleanly converted to the bis(TBA) salts which in turn by metathesis transformed, for example, into the corresponding disodium salt.

The electronic spectra of the dianions exhibited a rather broad absorption envelope between 275 and 375 nm with a maximum at 300-330 nm (see Table I). The increasing solvent polarity from CH_3CN to CH_3OH did not affect the absorption maxima of **2a**, but caused a small blue shift (4 nm) to **2h** and **2i**.

Bis(TBA) salts of **2** containing one or more dicyanomethylene groups showed two strong C≡N stretches between 2150 and 2197 cm^{-1} in the ir spectra,[10] while **2e**, **2g**, and **2h** without this group showed only one at 2170-2180 cm^{-1}, in-

Table I. Trimethylenecyclopropane Dianions (2)

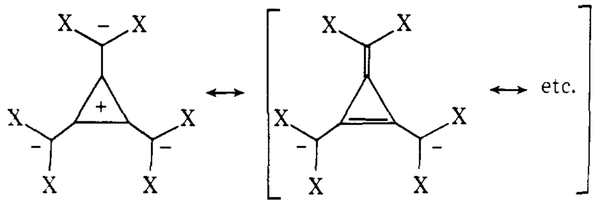


	X^1	X^2	X^3	X^4	X^5	X^6 [a]	% yield[b]	Uv Maxima in CH_3CN,[f] nm (ϵ)	Half-wave potentials (V) in CH_3CN vs. SCE E_1	E_2	$E_2 - E_1$
2a	CN	CN	CN	CN	CN	CN	94	315 (33 400), 285 sh (22 000), 222 (35 800)	+0.34	+1.13[h]	0.79
2b	CN	CN	CN	CN	CN	E	73	322 (34 400), 293 sh (24 700), 224 (32 600)	+0.26	+1.0	0.74
2c	CN	CN	CN	CN	E	E	38	322 (32 800), 269 (17 200), 223 (27 600)	+0.11[g]	—	—
2d	CN	CN	CN	E	CN	E	30	326 (37 500), 302 sh (24 100), 227 (30 000)	+0.17	+0.97	0.80
2e	CN	E	CN	E	CN	E	85	328 (39 200), 305 sh (29 700), 232 (32 300)	+0.10	+0.72	0.62
2f	CN	CN	E	E	E	E	40	315 (32 000), 268 (22 700)	+0.06[h]	+0.46[h]	0.40
2g	CN	E	CN	E	E	E	68[c]	320 (34 600), 305 sh (31 900), 234 (25 400)	+0.05[h]	+0.44[h]	0.39
2h	CN	E	E	E	E	E	69[d]	314 (38 500), 300 sh (35 000), 240 (>20 600)[j]	−0.01	+0.32[h]	0.33
2i	E	E	E	E	E	E	57[e]	309 (40 900), 264 (38 800)[k]	−0.07[i]	+0.16[i]	0.23

[a] E represents $COOCH_3$. [b] Not optimized; isolated as the bis(TBA) salt unless otherwise stated. [c] Isolated as the monohydrogen TBA salt. [d] In addition, the monohydrogen TBA salt was isolated in 21% yield. [e] Isolated as the diacid. [f] For the bis(TBA) salts. [g] Only one irreversible wave was observed. [h] Waves are not totally reversible. [i] The values were obtained by reduction of hexakis(methoxycarbonyl)TMCP.[5] [j] In 0.1 M TBA·OH−CH_3CN. λ_{max} (ϵ) in 0.1 M TBA·OH−CH_3OH 310 nm (36 200), 267 (22 100), 239 (22 200). [k] Conjugate diacid in 5 × 10^{-4} M TBA·OH−CH_3CN. λ_{max} (ϵ) in 0.1 M TBA·OH−CH_3OH 305 nm (38 600), 265 (32 200).

dicating strong mechanical coupling between the geminal cyano groups. The two ir-active C≡N stretches of the bis(TBA) salt of **2a** were also active in the Raman spectrum;[10] however, one was much stronger than the other. Comparison of these results with a fundamental vibrtion mode analysis indicated the expected D_{3h} symmetry for **2a.** In contrast, **2f–i** which contained more than four ester groups appeared to have nonplanar structures in which some ester groups were twisted out of the ring plane due to steric overcrowding, judging from the broadness and complexity of the carbonyl stretching bands. All the dianions showed a skeletal vibration[3a,11] in the ir spectra near 1420 cm^{-1}, that was also observed in the Raman spectra[12] of **2a** and **2i.** A Raman active and ir inactive skeletal vibration of the **2a** bis(TBA) salt appeared as a Fermi pair at 1915 and 1870 cm^{-1}. The corresponding band of the **2i** bis(TBA) salt was observed at 1880 cm^{-1}.

In the ^{13}C NMR spectrum, **2a** exhibited peaks at δ 124.5 (ring), 24.8 (methylene),[13] and 121.0 ppm (nitrile); the hexaester dianion **2i** at 138.4 (ring), 72.7 (methylene), 169.3 (carbonyl), and 49.3 ppm (methoxyl). If the ring carbon shifts are taken as a measure of π charge density,[14] the cyclopropenium **2A** contribution to the ground state may be estimated[15] as 8 and 30% for **2a** and **2i**, respectively. The estimates are consistent with the observed polar solvent effects on the electronic spectra and in qualitative agreement with the MO calculations.[4] The greater contribution of **2A** in the ground state of **2i** relative to **2a** again points to the steric overcrowding among the ester groups in **2i.**



2A **2B**

The polarographic data in Table I indicated that dianions **2** were oxidized in general by two one-electron processes to the radical anions **4** and the neutral species **5**. Although some oxidation waves were not reversible, it is evident that the first and second redox potentials as well as the difference between the two can be altered over a wide range by a proper choice of substituents. Thus, the hexaester **5i** is expected to be as electron deficient as TCNQ (−0.37, +0.17 V), but the radical anion **4i** would disproportionate more readily than that of TCNQ. The hexacyano compound **5a** will be one of the most potent π acids and should form a very stable radical anion.[5]

$$\underset{2}{[C_6X_6]^{2-}} \underset{+e}{\overset{-e}{\rightleftarrows}} \underset{4}{[C_6X_6]^{\cdot -}} \underset{+e}{\overset{-e}{\rightleftarrows}} \underset{5}{[C_6X_6]^{0}}$$

E_1 E_2

Acknowledgment. The author wishes to thank Drs. D. G. Swartzfager for the polarographic measurements, M. D. Gordon for the MO calculations, and D. W. Ovenall for the CMR studies.

References and Notes

(1) For recent articles on trimethylenecyclopropanes, see T. Bally and E. Haselbach, *Helv. Chim. Acta*, **58**, 321 (1975); E. A. Dorko, R. Sheps, and S. A. Rice, *J. Phys. Chem.*, **78**, 568 (1974).

(2) Triquinocyclopropandiides may be considered as an example of this class. R. West and D. C. Zecher, *J. Am. Chem. Soc.*, **92**, 161 (1970); R. West, D. C. Zecher, S. K. Koster and D. Eggerding, *J. Org. Chem.*, **40**, 2295 (1975).

(3) More pronounced perturbation is expected for the isoelectronic trisheterocyclopropenium ions which have been synthesized recently. (a) For a review, see Z. Yoshida, *Top. Curr. Chem.*, **40**, 48–72 (1973); (b) R. Gomper and U. Jersak, *Tetrahedron Lett.*, 3409 (1973); (c) Z. Yoshida, S. Miki, and S. Yoneda, *ibid.*, 4731 (1973).

(4) MO (PPP-CI) calculations on hexacyano-TMCP provided the following molecular parameters; π bond orders 0.362 and 0.775 for the ring and radial C–C bonds, charge densities +0.074, −0.019, +0.284, and −0.311 for the ring C, radial C, and nitrile C and N, respectively. The corresponding parameters for the dianion **2a** are 0.525, 0.506; +0.083, −0.319, +0.301, and −0.516.

(5) The oxidations of **2** to the radical anions and to the neutral species are reported in the accompanying communications: T. Fukunaga, M. D. Gordon, and P. J. Krusic, *J. Am. Chem. Soc.*, following paper in this issue.

(6) All new compounds analyzed satisfactorily.

(7) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **85**, 1179 (1963).

(8) Acetylacetone was also condensed successfully.

(9) Phenyl-, and benzoyl-, benzenesulfonylacetonitrile, and nitromethane could also be condensed with **3a.**

(10) All ir spectra were obtained as KBr pellets and Raman spectra as powder.

(11) (a) G. L. Closs, *Adv. Alicyclic Chem.*, 1, 53 (1966); (b) B. Schrader, *Angew. Chem., Int. Ed. Engl.*, **12**, 885 (1973).

(12) Raman spectra of other dianions have not been examined.

(13) The methylene carbon signal could be unambiguously observed only by judicious addition of chromium acetylacetonate. A paramagnetic reagent can reduce ^{13}C spin–lattice relaxation times and thus increases the sensitivity.

(14) The methylene carbon shifts do not appear to correlate with charge densities, but nuclear paramagnetic shieldings seem to be the dominant term. The methylene carbon shifts of malononitrile and methyl malonate are 9.0 and 41.4 ppm, respectively.

(15) The ring carbon shifts were compared with that of the cyclopropenium ion[16] (δ 177 ppm) assuming that the ^{13}C shift dependence on π charge (167 ppm/π electron[17]) is applicable.

(16) G. A. Olah, J. M. Bollinger, and A. M. White, *J. Am. Chem. Soc.*, **91**, 3667 (1969).

(17) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3419 (1975).

Tadamichi Fukunaga

*Contribution No. 2316, Central Research & Development
Department, E. I. du Pont de Nemours and Company
Experimental Station
Wilmington, Delaware 19898*

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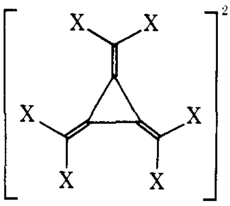
Negatively Substituted Trimethylenecyclopropanes and Their Radical Anions

Sir:

In the accompanying communication[1] we described the synthesis of trimethylenecyclopropanediides, **1**, fully substituted with cyano and/or ester groups. It was also shown that the dianions could be oxidized polarographically via radical anions, **2** to the neutral trimethylenecyclopropanes (TMCP), **3**. We wish to report here the oxidation products of these TMCP dianions.



$\equiv [C_6X_6]^{2-}$

1

$$\underset{1}{[C_6X_6]^{2-}} \underset{+1e}{\overset{-1e}{\rightleftarrows}} \underset{2}{[C_6X_6]^{\cdot -}} \underset{+1e}{\overset{-1e}{\rightleftarrows}} \underset{3}{[C_6X_6]^{0}}$$

a, X = CN; b. X = $COOCH_3$; c. X = H

The disodium salt of **1a** is cleanly oxidized with potassium persulfate in water to maroon, crystalline $K^+[C_6(CN)_6]^{\cdot -}$ in 95% yield.[2] The latter could be converted by metathesis to other simple 1:1 salts such as the tris(di-