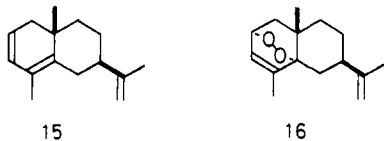


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 (17) (+)- α -Rotunol¹⁶ (**10b**) was prepared as follows. Treatment of tosylhydrazone of **2** with methylolithium gave diene **15** (73% from **2**), which on oxygenation with triplet oxygen in the presence of tungsten(VI) chloride (dark, -78°C , 2 h), followed by treatment of the resulting peroxide (**16**) with alumina (room



- temperature, 16 h), afforded α,β -unsaturated ketone, mp $102-104^\circ\text{C}$, $[\alpha]_D^{20} +53^\circ$ (CHCl_3) (88%), whose spectral data were identical with those of natural sample of **10b**. Cf. D. H. R. Barton, R. K. Haynes, P. D. Magnus, and I. D. Menzies, *J. Chem. Soc., Chem. Commun.*, 511 (1974).
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Received July 11, 1978

The Dianion of Dimethyl Cyclobut-3-ene-1,2-dicarboxylate. Aromaticity vs. Coulombic Repulsion

Sir:

That monocyclic anions and dianions containing $[4n + 2]$ π electrons are unusually stable and diatropic is now well authenticated. However, as the ring size decreases, the charge density per atom increases, and at high charge densities coulombic repulsion may become the dominant factor. Thus in small, multiply charged species, such as the cyclobutene dianion **1**, electron repulsion may outweigh the stabilization normally associated with the aromatic state. A number of attempts to prepare derivatives of **1** have been unsuccessful,^{2,3} but Pettit and co-workers⁴ provided evidence for the preparation of **1** itself by treatment of 3,4-dichlorocyclobutene with excess sodium naphthalide and quenching with MeOD, when 4% 3,4-dideuteriocyclobutene was isolated. We now report the preparation of the dimethyl cyclobut-3-ene-1,2-dicarboxylate dianion **3** and describe spectroscopic and chemical data which indicate that this anion does *not* benefit from aromatic delocalization.

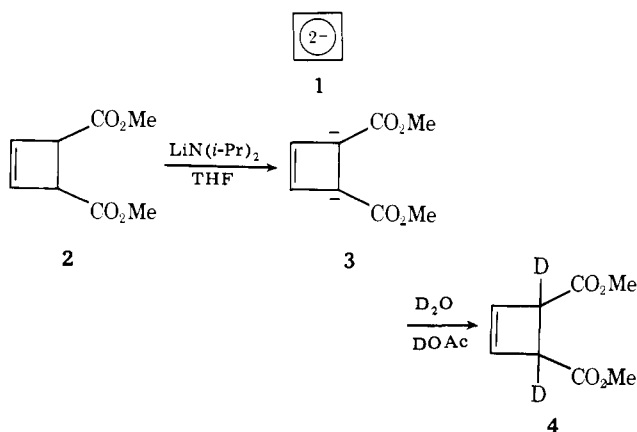
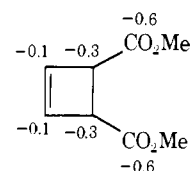
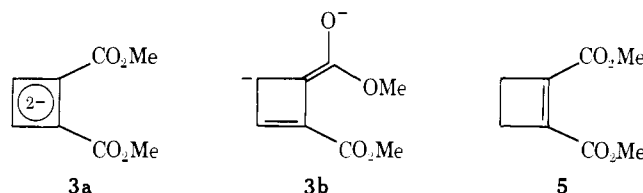


Chart I. Charge Distribution in **3**

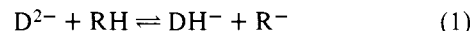


Addition of dimethyl cyclobut-3-ene-*cis*-1,2-dicarboxylate (**2**)⁵ to 2.5 equiv of $\text{LiN}(i\text{-Pr})_2$ in $\text{THF}-d_8$ at -75°C under argon gave a solution of the dianion **3**, stable at room temperature. The ^1H NMR spectrum showed two signals as broad singlets at δ 5.94 (2 H) and 3.73 (6 H),⁶ and the ^{13}C NMR spectrum showed signals at 150.4 ($\text{C}=\text{O}$), 121.1 (C-3,4), 93.2 (C-1,2), 53.6 and 50.9 (OCH_3). The ^{13}C NMR assignments are based on peak multiplicity under offset decoupling and selective decoupling of the methoxy protons.^{7,8} Addition of the dianion solution to rapidly stirred excess D_2O in dioxane containing 5 equiv of AcOD gave a 1:1 mixture of *cis*- and *trans*-dimethyl 1,2-dideuteriocyclobut-3-ene-1,2-dicarboxylate (**4**) in 50% yield.⁹ When the dianion was generated in the same way but in the presence of HMPA, quenching gave mainly (90%) *trans*-**4**.^{10,12} Comparison of the ^{13}C NMR chemical shifts of **3** with those of **2** and dimethyl cyclobut-1-ene-1,2-dicarboxylate (**5**),^{9,14} assuming a chemical-shift relationship of 160 ppm per electron,¹⁵ gave the charge distribution shown in Chart I, suggesting that 40% of the charge is located in the four-membered ring with 10% on C-3,4. The presence of two methoxy signals in the ^{13}C NMR spectrum of **3** reveals a substantial barrier to rotation of the methoxy groups between nonequivalent positions in the anion, a finding not unexpected from the charge distribution in the dianion and earlier observations by others.¹⁶

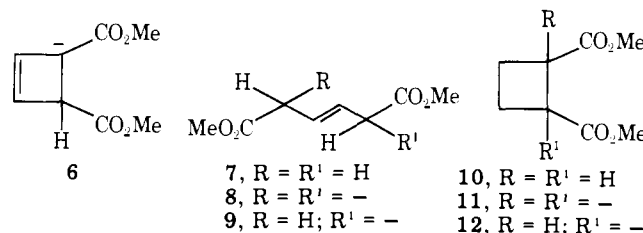
The ^1H NMR spectrum of **3** shows a small upfield shift of 0.27 ppm for the ring protons compared with that of the olefinic protons of **2**.^{12,17} This is somewhat less than would be predicted from the ^{13}C NMR charge densities (δ 1.0 assuming a chemical-shift relationship of 10 ppm per electron)¹⁸ and could be due to a small diatropic contribution from **3a**, to which the ^{13}C NMR spectrum is not susceptible.^{19,20} In order to quantify any



contribution from **3a**, the pK_a for the formation of the dianion **3** from the monoanion **6** was estimated by equilibration of **3** with hydrocarbons of known pK_a .



This pK_a value was then compared with those obtained in a similar manner for the formation of the dianions of dimethyl but-2-ene-1,4-dicarboxylate and dimethyl cyclobutane-1,2-dicarboxylate (**8** and **11**) from the corresponding monoanions



9 and **12**. Solutions of the dianions were prepared by adding the ester (1.0 mmol) in THF (0.5 mL) to $\text{LiN}(i\text{-Pr})_2$ (2.0

mmol) in a mixture of THF (1.0 mL) and HMPA (0.5 mL) at -75°C . After 30 min the reaction was warmed to -30°C and a hydrocarbon (0.5–0.8 mmol) of known pK_a was added in THF (1 mL) to the well-stirred solution. After 15 min the reaction mixture was cooled to -75°C and quenched by slow addition to a rapidly stirred mixture of D_2O , dioxane, and AcOD. Deuterium distribution was measured by mass and ^1H NMR spectra.

In the case of all three dianions virtually no deuterium ($\sim 0.05\text{D}$) was incorporated into the triphenylmethane ($pK_a = 31.5^{21}$) and the solutions showed little color change. With phenylxanthene (28.5^{21}) and fluorene (22.8^{21}) distinct color changes were observed with all three diester dianions. The fluorene was found to have incorporated 0.5D after equilibration with any of the three dianions, whereas phenylxanthene had incorporated 0.5, 0.37, and 0.15D when equilibrated with **3**, **8**, and **11**, respectively.²² When 0.5 equiv of triphenylmethane or phenylxanthene were used, the recovered diesters contained 1.4–1.6D,¹⁰ whereas upon treatment with 0.8 equiv of fluorene the diesters contained $\sim 0.95\text{D}$. Although only an estimate of the pK_a values of the three diester dianions can be made, since **10** is unstable under the equilibrium conditions and **8** is only partially soluble at -30°C , these data do suggest that all three dianions have a pK_a close to that of phenylxanthene (~ 28.5).^{23,24}

An increase in stability of the cyclic conjugated system over its acyclic analogue has been proposed as a criterion for determining the aromaticity of a molecule.^{27,28} Under such a criterion the dianion **3** is clearly *nonaromatic* since it is formed no more easily than its linear analogue **8**. One could consider, however, that **3** should be destabilized compared with **8** because of the greater enforced proximity of the two negative charges. That this does not follow is shown by the similar ease of formation of the dianion **11**, in which a similar charge proximity is required.

Does the nonaromaticity of **3** allow any comment to be made about the aromaticity of the parent dianion **1**? Cyanocyclopentadiene has a pK_a of 10, whereas cyclopentadiene has a pK_a of 16 and acetonitrile a pK_a of 25.^{25,29} Clearly in this case the conjugative and cyclic delocalization effects are supportive. Similarly, the kinetic acidity of 3-cyano-1,2-diphenylcyclopropane is 10^4 less than that of 3-cyano-1,2-diphenylcyclopropane,²⁸ in this case the effects being opposed because of the antiaromaticity of the cyclopropenyl anion. Since the pK_a for formation of dianion **8** is known, any supportive cyclic delocalization effect in dianion **3** should be reflected in a significant decrease in its pK_a value. The lack of such an effect strongly supports the inference that **1** is nonaromatic.

Acknowledgments. We thank the Science Research Council, U.K., for support, Dr. A. G. Loudon for advice on obtaining the mass spectra, and BASF (Ludwigshafen) for a gift of cyclooctatetraene.

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- ^{13}C NMR, THF- d_6 , C_6H_6 internal standard, offset decoupled; 150.4 (singlet), 121.1 (doublet), 93.2 (singlet), 53.6–50.9 (broad multiplet).
- For ^{13}C NMR spectra of other dianions of organic systems see J. B. Lambert and S. M. Wharry, *J. Chem. Soc., Chem. Commun.*, 172 (1978).
- ^{13}C NMR (CDCl_3 , C_6H_6 internal standard): *cis*-**2**, 170.7 (C=O), 136.3 (C-3,4), 51.5 (OMe), 48.5 (C-1,2); *trans*-**2**, 171.1 (C=O), 136.9 (C-3,4), 51.6 (OMe), 48.5 (C-1,2); **5**, 160.4 (C=O), 141.5 (C-1,2), 50.7 (OMe), 26.2 (C-3,4).
- Quenching **3**, prepared in either THF or THF–HMPA, gave **4** containing $\sim 1.5\text{D}$ (10% D_0 , 30% D_1 , 60% D_2) by mass spectrum. The presence of mono- and nondeuterated ester is due to competitive diffusion controlled incorporation of acidic protons already present in the reaction medium. This problem has been previously encountered.¹¹ No trideuterated ester was obtained when the dianion **8** was quenched in an identical fashion, demonstrating that exchange does not occur under these conditions.
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- Deuteration of fluorene is probably incomplete because of competitive protonation from the reaction medium.¹⁰ The deuterated fluorene contained $\leq 3\%$ D_2 ; so subsequent exchange has not occurred on quenching.
- Reaction of **8** with phenylxanthene at -30°C , followed by warming to 0°C and then quenching, gave the same deuterium distribution, indicating that equilibrium had been achieved.
- The pK_a of ethyl acetate in water is reported as 24.5²⁵ which can be converted to a value of ~ 29.5 in Me_2SO .²⁶ This suggests that 1,2-diester dianions may be much more readily prepared than is generally assumed.
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Received June 12, 1978

An N–S Bonded Cation Radical $[\text{R}_3\text{N–SR}_2]^{\cdot+}$ and a Dication $[\text{R}_3\text{N–SR}_2]^{2+}$ from 5-Methyl-1-thia-5-azacyclooctane

Sir:

We previously reported the formation of a long-lived thioether cation radical which was stabilized by a transannular thioether group.¹ At that time we suggested that other lone-pair donors might be capable of stabilizing a thioether cation radical if no steric or electronic effects prevented a transannular interaction. We now have formed both a long-lived N–S bonded cation radical and a dication of the mesocyclic amino thioether, 5-methyl-1-thia-5-azacyclooctane (I).

Although aliphatic cation radicals and dications having the same heteroatoms bonded together are known, i.e., hydrazines,² tertiary amines,³ dithioethers,⁴ diphosphites,⁵ and diselenoethers,⁶ this is the first example of an aliphatic cation radical and dication in which two *different* heteroatoms are bonded together.

The mesocyclic amino thioether I was prepared by the method of Yethon.⁷ When I was oxidized with 2 equiv of NOBF_4 in propionitrile, 2 equiv of NO was evolved. The