Table I. ^{13}C NMR Data for 2a–d

	C-1,4	C-2,3	C-5,8	C-6,7	C-9,10	C-8a,I0a	C-4a,9a	other
2a[a]	200.8	35.7	124.4	130.4	154.9	129.1	107.3	
2b[b]	149.5 (s)[c]	20.0 (t)	122.3 (d)	125.9 (d)	146.5 (s)[c]	125.3 (s)	108.0 (s)	
2c[d]	148.2[c]	20.1	122.2	125.3	146.2[c]	125.8	107.5	30.72[e]
2d[b,f]	164.4 (s)	23.1 (t)	123.9 (d)	128.1 (d)	154.5 (s)	128.0 (s)	106.1 (s)	*g*, *h*

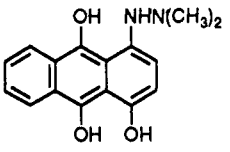
[a] $CDCl_3$.[5] [b] DMSO-d_6, proton coupled. [c] Assignments may be reversed. [d] DMSO-d_6, proton decoupled. [e] Methyl group bonded to nitrogen. [f] Reference 9 reports data for $(CH_3)_2C{=}NN(CH_3)_2$, azines, and other hydrazones. [g] $-N{=}C(CH_3)_2$ (q) for anti CH_3 at 25.62; (q) for syn CH_3 at 18.96. See ref 9. [h] $-C{=}N(CH_3)_2$, 166.07 for hydrazone carbon, may be reversed with C-1,4.

acterize. On the other hand, when **2a** was refluxed in methylhydrazine, 1,4-diaminoanthracene-9,10-dione (**1e**) was obtained (30%).

Treatment of **2a** with *N,N*-dimethylhydrazine at room temperature led to 1-amino-4-hydroxyanthracene-9,10-dione (**1f**; 59%). A small amount of the desired bis(hydrazine) **1a** (10%) was also isolated. In this case, the same **1f**:**1a** product ratio also resulted if the reaction was conducted at reflux.

While the formation of hydrazones **2b** and **2c** is unexceptional, the observation that they exist predominantly as these tautomers is of interest.

A N–N bond cleavage of a hydrazine intermediate has been found in the conversion of a 1,2,3,4-tetrahydro-β-carboline to a 4-amino-β-carboline.[10] A mechanism has been proposed for this transformation. In the formation of **1f** from *N,N*-dimethylhydrazine and **2a**, an intermediate such as **4** might be involved which could undergo a N–N bond cleavage to **5** followed by a tautomerization to **1f**.



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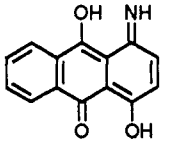

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The formation of the double N–N cleavage product **1e** from **2a** and methylhydrazine is interesting, but mechanistic speculation about its formation would appear to be unwarranted at this time.

Experimental Section

Melting point were determined on a Thomas-Hoover apparatus and are uncorrected. ^1H NMR were run on a Bruker WM-250 pulsed Fourier transform spectrometer. TLC precoated silica gel plates (Eastman chromagram sheets with fluorescent indicator) were used to monitor reactions. For column chromatography Baker analyzed 80–200-mesh silica gel was utilized. Microanalyses were performed by Robertson Laboratories, Madison, NJ.

2,3-Dihydro-9,10-dihydroxy-1,4-anthracenedione Bis(hydrazone) (2b). Leucoquinizarin (**2a**; 1 g, 4.1 mmol) and anhydrous hydrazine (24 g, 757 mmol) were stirred at room temperature under nitrogen for 3.5 h. The reaction mixture was poured into brine and filtered to yield a brownish solid (1.02 g, 91%). Analysis by TLC (silica gel, 95% $CHCl_3$/MeOH) showed one major yellow spot, a minor red spot, and traces of other components: ^1H NMR (DMSO-d_6) δ 2.77 (s, 4 H), 6.68 (s, 4 H), 7.45 (m, 2 H), 8.15 (m, 2 H), 14.32 (s, 2 H).

Column chromatography (silica gel, 95% $CHCl_3$/MeOH) of 210 mg of the crude product gave a yellow solid (100 mg) and a red uncharacterized solid (20 mg). The yellow solid changed to red on standing in air for 1 day and had an ^1H NMR similar to that of the crude reaction product.

Bis(acetone hydrazone) 2d. Crude **2b** (212 mg, 0.78 mmol) was refluxed in acetone (20 mL) for 4 h. Crystalline purple needles were collected upon cooling (177 mg, 65%) and were identified as **2d**: ^1H NMR ($CDCl_3$) δ 2.01 (s, 6 H), 2.20 (s, 6 H), 3.25 (s, 4 H), 7.6 (m, 2 H), 8.4 (m, 2 H), 15.34 (s, 2 H); mp 208–211 °C. Anal. Calcd for $C_{20}H_{22}N_4O_2$: C, 68.57; H, 6.28; N, 16.00. Found: C, 68.34; H, 6.51; N, 15.73.

2,3-Dihydro-9,10-dihydroxy-1,4-anthracenedione Bis(2-methylhydrazone) (2c). Leucoquinizarin (**2a**; 0.5 g, 2.1 mmol) and methylhydrazine (8.7 g, 190 mmol) were stirred at room temperature for 18 h. The mixture was poured into saturated brine, and a brown solid was collected (0.5 g, 80%). Analysis by TLC (silica gel, $CHCl_3$) showed the presence of a major yellow compound: ^1H NMR (DMSO-d_6) δ 2.79 (s, 4 H), 2.99 (s, 6 H), 6.59 (s, 2 H), 7.48 (m, 2 H), 8.15 (m, 2 H), 14.08 (s, 2 H); mp 120–128 °C (attempts at purification led to decomposition).

1,4-Bis(*N,N*-dimethylhydrazino)anthracene-9,10-dione (1a) and 1-Amino-4-hydroxyanthracene-9,10-dione (1f). (a) Reflux Conditions. Leucoquinizarin (**2a**; 500 mg, 2 mmol) and *N,N*-dimethylhydrazine (4.0 g, 16 mmol) were stirred at reflux under nitrogen for 4 h. The mixture was poured into ice–water, and a purple solid (510 mg) was collected. A 200-mg portion of this crude solid was crystallized from benzene to yield dark red needles with a greenish metallic luster of **1f**: 116 mg, 59%; mp 208–209 °C (lit.[11] mp 206 °C); ^1H NMR ($CDCl_3$) δ 7.01 (d, 1 H), 7.20 (d, 1 H), 7.80 (m, 2 H), 8.35 (m, 2 H), 13.56 (s, 1 H). Analysis of the crude product by TLC (silica gel, $CHCl_3$) indicated the presence of yellow, blue, and red components (**1f**). Chromatography ($CHCl_3$, silica gel) yielded a yellow compound, which was not characterized, and a blue compound was identified as **1a**: 10%; mp 152–154 °C (EtOH/H_2O); ^1H NMR ($CDCl_3$) 2.69 (s, 12 H), 7.72 (m, 2 H), 7.95 (s, 2 H), 8.30 (m, 2 H), 10.98 (s, 2 H). Anal. Calcd for $C_{18}H_{20}N_4O_2$: C, 66.64; H, 6.21; N, 17.28. Found: C, 66.48; H, 6.14; N, 17.08. The red component **1f** was also isolated.

(b) Room-Temperature Conditions. Leucoquinizarin (**2a**; 1 g, 4.1 mmol) and *N,N*-dimethylhydrazine (12 g, 197 mmol) were stirred at room temperature for 19 h. The mixture was poured into brine to yield a purple solid (1 g). Analysis by TLC and R_f comparisons showed **1a** and **1f** to be present. Analysis by ^1H NMR ($CDCl_3$) indicated a **1a**:**1f** ratio of 1:2.8.

1,4-Diaminoanthracene-9,10-dione (1e). Leucoquinizarin (**2a**; 300 mg, 1.24 mmol) was refluxed in methylhydrazine (3 mL) for 4 h under nitrogen. The purple solution was poured into brine, and a purple solid (295 mg) was collected. Crystallization from pyridine/water gave **1e**: 89 mg, 30%; mp 247–251 °C (lit.[12] mp 263 °C); ^1H NMR δ 6.91 (s, 2 H), 7.07 (s, 4 H), 7.71 (m, 2 H), 8.33 (m, 2 H).

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On the Resonance Energy of Methylenecyclopropene and Cyclopropenone

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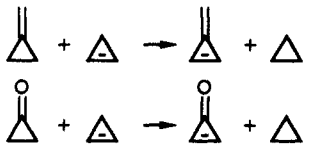
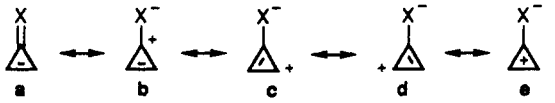
The aromaticity of methylenecyclopropene (**1**) and cyclopropenone (**2**) have been discussed and debated over many years.[1-8] The arguments revolve about the defi-

nition of the term aromaticity.[9] Recently, Staley and co-workers detailed a list of criteria that can be used to quantify the aromaticity of **1** and **2**.[7,8] One criterion is the resonance energy (RE), defined as the energetic stabilization relative to appropriate reference molecules. Staley[7,8] and others[2,5,6] have used the energy of reaction 1 and 2 to indirectly predict the RE of **1** and **2**, respectively. We present here an analysis of the assumptions inherent in these reactions.



The RE in these systems is thought to arise from the interaction of the two π bonds in their T-arrangement, leading to the resonance structures **1a–e** and **2a–e**. The



1: X = CH_2
2: X = O

reference system is chosen such that it contains all the structural and electronic features of **1** and **2** without any of the charged resonance structures. For **1**, the reference system is methylenecyclopropane and cyclopropene (reaction 1), where the two π bonds are isolated but present in a structural environment similar to **1**. Analogously, the reference **2** is cyclopropanone and cyclopropene (reaction 2). Unfortunately, the energies of these isodesmic reactions do not directly yield the RE.

Both **1** and **2** contain ring strain energy (RSE) that must be accounted for in order to determine the RE alone. For these systems, a reference that separates RE from RSE cannot be constructed. Instead, the claim is made that the RSE of **1** is approximately equal to the RSE of methylenecyclopropane and cyclopropene less the RSE of cyclopropane;[5] however, evaluation of this claim is impossible. Further, Staley[8] has shown in-plane π ("σ") delocalization stabilizes these molecules, but again the energy associated with this stabilization cannot be evaluated. Therefore, the isodesmic reaction energies of reactions 1 and 2 include some unknown energetic contribution due to these effects,

Table I. Groups and Their Energy Equivalents (in kcal mol^{-1}) for Reactions 1 and 2

reactants			products		
group	number present	ΔH_f	group	number present	ΔH_f
		Reaction 1			
C_d-(H)2	1	6.26	C_d-(H)2	1	6.26
C_d-(C)2	1	10.34	C_d-(C_d)2	1	7.2
C-(C_d)(C)(H)2	2	-4.76	C_d-(C_d)H	2	6.78
C_d-(C_d)(H)	2	8.59	C-(C)2(H)2	3	-4.95
C-(C_d)2(H)2	1	-4.29			
total		19.97	total		12.17
		ΔH(rxn) = -7.80			
		Reaction 2			
(CO)-(C)2	1	-31.5	(CO)-(C_d)$_2$	1	-39.1
C-(CO)(C)(H)2	2	-5.0	C_d-(CO)(H)	2	7.7
C_d-(C)(H)	2	8.59	C-(C)2(H)2	3	-4.95
C-(C_d)2(H)2	1	-4.29			
total		-28.61	total		-38.55
		ΔH(rxn) = -9.94			

which must be deducted from the reaction energy to yield the RE.[5,7,8]

Staley calculated the energies of reaction 1 and 2 at the MP2/6-31G* level.[7,8] The energies are -8.5 kcal mol^{-1} for reaction 1 and -24.1 kcal mol^{-1} for reaction 2. Similar values have been reported at various other calculational levels.[2,8] Based on these energies, and primarily geometric and charge distribution considerations, Staley concluded that **1** is nonaromatic[7] and **2** is moderately[8] aromatic. However, the isodesmic reaction energies, even with the consideration of RSE and "σ" delocalization seem to indicate anomalously large REs.

Careful examination of reactions 1 and 2 reveals that while these are isodesmic reactions, they do not conserve groups as defined by Benson.[10] For example, C3 of methylenecyclopropane is classified by Benson as C_d-(C)2, having an energy equivalent of 10.34 kcal mol^{-1}. This carbon should correspond with C3 of methylenecyclopropene, which belongs to a C_d-(C_d)2 group. We estimate the energy of the C_d-(C_d)2 group to be 7.2 kcal mol^{-1} based on the equivalents C_d-(H)2, 6.26 and C_d-(C_d)(H), 6.78. The energy for reaction 1, using only the Benson equivalents and neglecting any RSE corrections, is -7.8 kcal mol^{-1}. The details of this calculation are given in Table I. This energy, an estimation of the energetic consequences due solely to regrouping the atoms, also must be deducted from the calculated reaction energy to obtain the RE of **1**. This leads to a revised isodesmic reaction energy of -0.7 kcal mol^{-1}, suggesting a small RE, in agreement with geometric and charge distribution arguments presented by Staley.[7]

Similar analysis can be applied to reaction 2. Here the carbonyl of cyclopropanone, (CO)-(C)2 (-31.5 kcal mol^{-1}), must correspond with the carbonyl of **2**, (CO)-(C_d)2. We estimate the energy of the (CO)-(C_d)2 group to be -39.1 kcal mol^{-1} based on the equivalent for (CO)-(C_B)2, -39.1 kcal mol^{-1}. The reaction energy for reaction 2, based on the Benson equivalents alone, is -10 kcal mol^{-1} (see Table I). Subtracting this energy from the calculated reaction energy of -24.1 kcal mol^{-1} leads to the revised reaction energy of 14 kcal mol^{-1}. Assuming that this corrected energy reflects the RE, the geometric, charge distribution, and RE arguments consistently indicate moderate aromaticity in **2**.[8]

We recently proposed the group equivalent reaction[11] as a method for constructing balanced chemical reactions

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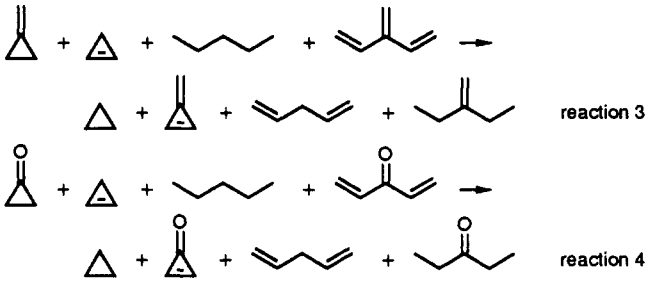
to measure such quantities as RE and RSE. This reaction conserves groups as defined by Benson and gives a reaction that minimizes the structural differences between reactant and product. Possible group equivalent reactions to obtain the RE of **1** and **2** are given in reactions 3 and 4, respectively. Unfortunately, these reactions involve fairly sizable



molecules that will tax most computational resources. However, if care is excercised in utilizing simple reactions and one corrects for nonconservation of chemical groups, quite reasonable estimates of RE can be readily calculated.

Registry No. **1a**, 4095-06-1; **2a**, 2961-80-0.

A New Synthetic Route to 1,1,2,2-Tetracyanocyclopropanes

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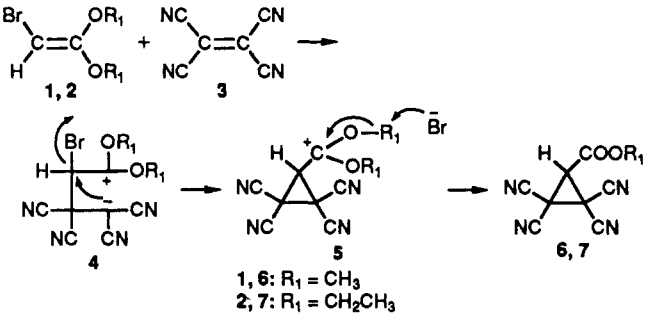
1,1,2,2-Tetracyanocyclopropane can be prepared rather easily by reaction of aqueous formaldehyde and malononitrile[1] or tetracyanoethylene with diazomethane.[2] A large number of substituted 1,1,2,2-tetracyanocyclopropanes are available by the Wideqvist reaction,[3,4] in which a carbonyl compound reacts with 2 equiv of bromomalononitrile. A similar cyclopropanation procedure was reported by Hart.[5,6]

In a previous report, we described the rather unexpected formation of a cyclopropane ring in the reaction of 1,1-diethoxy-2-bromoethylene with ethyl α-cyanoacrylate.[7] A zwitterionic tetramethylene is formed by reaction of the electron-rich olefin with the electron-poor olefin. The expected cyclobutane cycloadduct was not formed. Instead, elimination of the bromide anion takes place with formation of a cyclopropane ring. Dealkylation of the dialkoxycarbocation by Br^- leads to an ester substituent. A similar reaction has been described by Scheeren: β,β-dicyanostyrene with 1,1-diethoxy-2-chloroethylene also yields a cyclopropane derivative as a reaction product.[8]

In the present work, we react bromoketene acetals with tetracyanoethylene to form tetracyanocyclopropanecarboxylates.

Results and Discussion

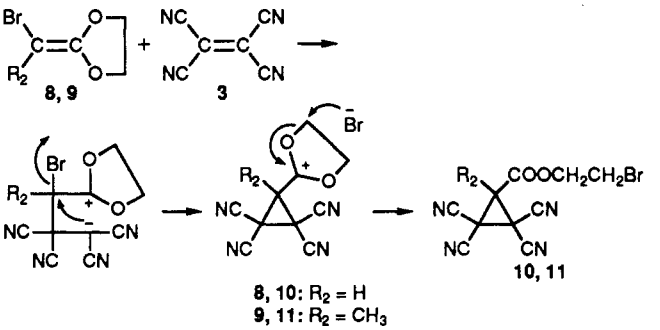
1,1-Dialkoxy-2-bromoethylenes **1** or **2** react with tetracyanoethylene (TCNE, **3**) at −10 °C to form methyl or ethyl 2,2,3,3-tetracyanocyclopropanecarboxylate (**6** or **7**), respectively. In analogy to the α-cyanoacrylate case,[7] the following mechanism is proposed. The initially formed



1,4-zwitterion **4** undergoes intramolecular elimination of bromide to form the dialkoxy cation **5**, which in turn undergoes dealkylation to form cyclopropane (**6**, **7**) and alkyl bromide. When the reaction is carried out in THF as solvent, a large quantity of poly-THF is formed together with the desired cyclopropane. This is additional evidence for the formation of a 1,4-zwitterion in the course of reaction, which can initiate the cationic polymerization of THF.[9]

1,1-Diethoxy-2-bromopropene was much less reactive than 1,1-diethoxy-2-bromoethylene. Even at room temperature, no reaction occurred when 1,1-diethoxy-2-bromopropene was mixed with TCNE in a 1:1 molar ratio in THF.

Cyclic ketene acetals also undergo the reaction. When 2-(bromomethylidene)-1,3-dioxolane (**8**) or 2-(bromoethylidene)-1,3-dioxolane (**9**) reacts with TCNE, a high yield of 2-bromoethyl 2,2,3,3-tetracyanocyclopropanecarboxylate **10** or **11** is obtained. The cyclic ketene acetal **8** has a tendency to undergo spontaneous cationic polymerization and the cyclopropane was always contaminated by the homopolymer of **8**. In this case, the extra methyl



group on the double bond of the ketene acetal did not reduce the reactivity significantly.

All 2,2,3,3-tetracyanocyclopropanecarboxylates (**6**, **7**, **10**, **11**) were very sensitive to base or nucleophile. Saponification to carboxylic acid has failed so far. Even weak bases, such as silver acetate, attacked the ring or the cyano groups. We were unable to obtain the vinyl ester derivatives in attempted dehydrobrominations of **10** and **11**.

Experimental Section

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus. ^1H NMR and ^{13}C NMR spectra were taken on a Bruker WM 250 nuclear magnetic resonance spec-

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