α to C=O), 3.21, 3.23 (2 s, 6 H, 2 MeN$^+$), 3.60 (m, 3 H, CH$_2$N + 1 OC*H*$_2$CH), 3.97 (m, 4 H, N$^+$CH$_2$CH$_2$O), 4.47 (m, 1 H, 1 OC*H*$_2$CH), 5.64 (m, H, OCH$_2$C*H*). The OH signal was not observed.

Anal. Calcd for $C_{39}H_{78}O_5NBr$: C, 64.9; H, 10.9; N, 1.94. Found: C, 64.9; H, 11.2; N, 1.76.

(1,2-Bis(palmitoyloxy)-3-propyl)dimethyl(β-(*p*-nitrophenyl carbonato)ethyl)ammonium Bromide (2). To a solution of 350 mg (0.49 mmol) of **6** in 15 mL of freshly distilled CHCl$_3$ was added 400 mg (1.98 mmol) of *p*-nitrophenyl chloroformate and 39 mg (0.49 mmol) of dry pyridine (distilled from KOH and BaO). The solution was stirred magnetically for 60 h at 25 °C in a flask protected from moisture. Solvent was stripped, and the solid residue was recrystallized from acetone. Traces of pyridinium hydrochloride were removed by percolation with 5 mL of cold water (pH 5.5). The solid was dried under vacuum to give 250 mg (0.28 mmol; 57%) of carbonate **2**: R_f = 0.3 (TLC on silica gel, 9:1 CHCl$_3$/MeOH); mp ~105 °C (gel), 150 °C (dec); NMR (400 MHz, 70:30 CDCl$_3$, CD$_3$OD) δ 0.82 (crude t, $J \sim 7$ Hz, 6 H, 2 CH$_3$), 1.2 ("s", 48 H, 2 (CH$_2$)$_{12}$), 1.53 (m, 4 H, 2 CH$_2$ β to C=O), 2.27 (m, 4 H, 2 CH$_2$ α to C=O), 3.25, 3.27 (2 s, 6 H, 2 MeN$^+$), 3.76 (m, 2 H, CHC*H*$_2$N$^+$), 4.02 (m, 4 H, N$^+$CH$_2$CH$_2$O), 4.40 (d, J = 7 Hz, 1 H, 1 OC*H*$_2$CH), 4.70 (s, 1 H, 1 OC*H*$_2$CH) 5.56 (m, 1 H, OCH$_2$C*H*), 7.40 and 8.22 (A$_2$B$_2$ "doublets", 4 H, aromatic).

Anal. Calcd for $C_{46}H_{81}O_9N_2Br$: C, 62.3; H, 9.22; N, 3.16; Br, 9.02. Found: C, 62.3; H, 8.93; N, 2.95; Br, 9.25.

Generation of Vesicles. **2** (3.15 mg) was placed in a 50-mL beaker with 25 mL of distilled water adjusted to pH 3.92 with HCl. The water was added so that all of the solid was under water, with none floating on the surface. The beaker was put in a water bath at 20 °C, and after 5 min, its contents were sonicated with the 108 mm × 19 mm (diameter) immersion probe of the Braunsonic Model 1510 sonicator. The sonicator probe was immersed to three-fourths of its length, and sonication at 40 W was carried out for 25 min, during which the temperature of the solution rose to 38 °C. The vesicle solution was cooled to ~20 °C and filtered through a 0.8-μm Millex (Millipore) filter. See above for physical characterization of vesicular **2**.

Light Scattering. Light scattering data were collected at 25 °C and a 90° scattering angle with a Nicomp Model TC-100 computing autocorrelator, an argon laser light source (488 nm), and a Hazeltine microcomputer that used the cumulant program. The channel width was adjusted to produce a decay of 1.5–2.0 s. Vesicles were generated as described above, using [**2**] = 5×10^{-5} M. Variance in the observed hydrodynamic diameter ranged from 0.4–0.7. A variance <1.0 indicates a unidisperse system.

Electron Microscopy. One drop of a 5×10^{-5} M aqueous solution of vesicular **2**, prepared at pH 3.9, was placed on a 200-mesh carbon–formvar coated copper grid. One drop of 2% aqueous uranyl acetate (pH 4) was added. After 2 min, excess liquid was carefully blotted, and the sample was air-dried for 5–10 min more. The specimen was examined with a JEOL 100CX electron microscope at 80 kV. Micrographs were recorded at magnifications of 50 000 and 66 000.

T_c Measurement. To 3.15 mg (0.0036 mmol) of **2** in a 50-mL beaker was added 5 μL of a 1×10^{-5} M THF solution of 1,6-diphenyl-1,3,5-hexatriene (Fluka). Solvent was removed in a stream of nitrogen, and 25 mL of a pH 3.9 (HCl) solution of 0.01 M KCl was added. Sonication and filtration were carried out as described above. Fluorescence polarization measurements were carried out on 2–3-mL samples as described in ref 11, using a Perkin-Elmer Model MPF-3L fluorescence spectrometer and Polacoat 4B polarizers for both excitation and emission beams. Temperature (±1 °C) was regulated by a thermostated, circulating-water bath. The data appear in Figure 1 and are interpreted in the Discussion.

Kinetic Methods. Reactions were initiated by mixing vesicle solutions with Tris buffer solutions at various pHs. Kinetics were followed at 400 nm (PNPO$^-$ release) on a Gilford Model 250 spectrophotometer and a Gilford Model 6051 recorder. Pseudo-first-order rate constants were obtained from the traces by computer analysis in the standard manner. Kinetic runs are summarized in Table I.

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Structural Studies of 4-Phenyl-2,4,6-triazatetracyclo[6.3.2.0^{2,6}.0^{7,9}]trideca-10,12-diene-3,5-dione, a Dihydrodiazabullvalene. Preference for a Bisected Aminocyclopropane Derivative Having an Unusual Planar Triazolidinedione Ring

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Abstract: X-ray structural analyses of dihydrodiazabullvalene derivative **2** have disclosed a nearly planar triazolidinedione ring. This geometry corresponds to a bisected aminocyclopropane with a planar amino group; prior calculations indicated this to be the least stable geometry for an aminocyclopropane. The analyses also reveal a long distal cyclopropyl bond of 1.688 (4) Å at 293 K or 1.586 (2) Å at 153 K with shorter adjacent cyclopropyl bonds of average value 1.477 (3) Å at 293 K or 1.499 (2) Å at 153 K. The long distal bond length at 293 K is associated with a high degree of atomic thermal motion. σ-Acceptor effects associated with the electronegative N3 atom of the triazolidinedione best account for distortions of the cyclopropyl bond lengths. Interatomic distances revealed by the X-ray diffraction analyses of crystalline **2** are consistent with a static structure, which at 293 K shows a step in the progression to the fluxional state; **2** is fluxional in solution at 30 °C.

The [4 + 2]-cycloaddition product **1** of 4-phenyl-1,2,4-triazoline-3,5-dione and cyclooctatetraene has been reported to form a photoproduct upon acetone-sensitized irradiation.[1] A rearranged dihydrodiazabullvalene **2** was suggested; however, confirming spectral data for **2** were not reported.[1,2] Further investigation

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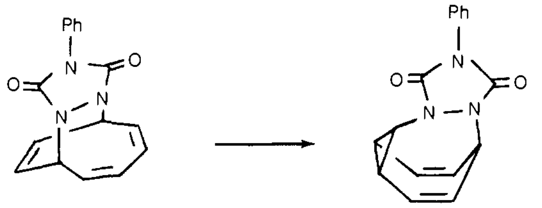

1 2

of the structural parameters of **2** seemed to be of interest because of its relationship to azabullvalenes[3] and similar homotropilidenes[4] which show fluxional behavior, because of concerns about the geometrical consequences of the interaction of cyclopropanes with adjacent "lone-pair" substituents,[5-8] and in light of recent studies of substituent effects upon the deviation from planarity of triazolidinedione structures, which have been used to probe nitrogen inversion pathways.[9]

Figure 1. Depiction of geometries of bisected and trans, pyramidal aminocyclopropane.

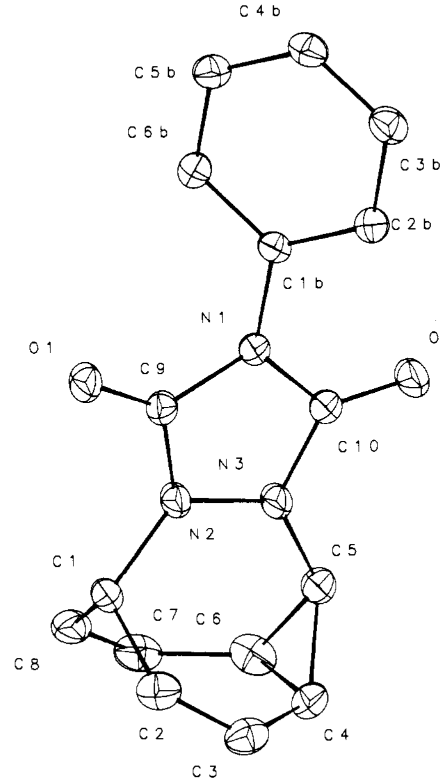

Figure 2. ORTEP diagram and numbering pattern for **2**.

The nitrogen atom adjacent to the cyclopropyl ring in **2** is constrained to a bisected planar conformation (Figure 1), if trigonally hybridized ($N(sp^2)$), or to a variant of the bisected conformation, if tetrahedrally hybridized ($N(sp^3)$).[5b] Some predictions regarding the bond angles and bond lengths in **2** are possible. First, the microwave structure determination for cyclopropylamine indicates a symmetrical pyramidal conformation with the NH_2 hydrogens trans to the cyclopropyl ring to be most stable (Figure 1).[8a] Model calculations with the amino group held planar indicate the bisected isomer to be the least stable conformer, 3.9 kcal/mol higher than the lowest energy (trans, pyramidal) conformation.[5a] The ring distortion of the bisected conformer, while not very pronounced, is characteristic of a weak σ acceptor, and the prediction is that in this conformer the adjacent cyclopropyl bonds are shortened and the distal cyclopropyl bond is lengthened relative to those of cyclopropane.[5a,6]

Second, in the bisected planar conformation, the sum of the bond angles for the nitrogen adjacent to cyclopropane should be

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Table I. Bond Distances and Bond Angles for Dihydrodiazabullvalene **2**[a]

T = 293 K									
Distances, Å									
O1–C9	1.212 (2)	O2–C10	1.210 (2)	N1–C9	1.394 (2)	N1–C10	1.397 (3)
N1–C1b	1.427 (2)	N2–N3	1.393 (2)	N2–C1	1.458 (3)	N2–C9	1.352 (3)
N3–C5	1.426 (3)	N3–C10	1.350 (3)	C1–C2	1.483 (4)	C1–C8	1.510 (4)
C2–C3	1.333 (4)	C3–C4	1.418 (4)	C4–C5	1.482 (3)	C4–C6	1.688 (4)
C5–C6	1.472 (3)	C6–C7	1.423 (4)	C7–C8	1.301 (4)	C1b–C2b	1.390 (3)
C1b–C6b	1.375 (3)	C2b–C3b	1.391 (3)	C3b–C4b	1.374 (4)	C4b–C5b	1.377 (3)
C5b–C6b	1.386 (3)	C1–C5	2.999 (3)[b]	C2–C8	2.337 (4)[b]	C3–C7	3.026 (3)[b]
Angles, deg									
C9–N1–C10	110.9 (2)	C9–N1–C1b	123.9 (2)	C10–N1–C1b	125.1 (2)	N3–N2–C1	122.3 (2)
N3–N2–C9	109.4 (2)	C1–N2–C9	126.7 (2)	N2–N3–C5	124.7 (2)	N2–N3–C10	109.7 (2)
C5–N3–C10	125.4 (2)	N2–C1–C2	114.6 (2)	N2–C1–C8	112.8 (2)	C2–C1–C8	102.7 (2)
C1–C2–C3	126.0 (2)	C2–C3–C4	126.6 (2)	C3–C4–C5	124.0 (2)	C3–C4–C6	117.7 (2)
C5–C4–C6	54.9 (2)	N3–C5–C4	121.1 (2)	N3–C5–C6	122.8 (2)	C4–C5–C6	69.7 (2)
C4–C6–C5	55.4 (2)	C4–C6–C7	118.4 (2)	C5–C6–C7	126.9 (3)	C6–C7–C8	127.1 (2)
C1–C8–C7	124.3 (2)	O1–C9–N1	127.9 (2)	O1–C9–N2	127.1 (2)	N1–C9–N2	105.0 (2)
O2–C10–N1	127.7 (2)	O2–C10–N3	127.5 (2)	N1–C10–N3	104.8 (2)		
T = 153 K									
Distances, Å									
O1–C9	1.226 (1)	O2–C10	1.221 (2)	N1–C9	1.404 (2)	N1–C10	1.405 (2)
N1–C1b	1.426 (2)	N2–N3	1.401 (2)	N2–C1	1.468 (2)	N2–C9	1.361 (2)
N3–C5	1.430 (2)	N3–C10	1.358 (2)	C1–C2	1.510 (2)	C1–C8	1.516 (2)
C2–C3	1.338 (2)	C3–C4	1.474 (2)	C4–C5	1.500 (2)	C4–C6	1.586 (2)
C5–C6	1.498 (2)	C6–C7	1.469 (2)	C7–C8	1.332 (2)	C1b–C2b	1.395 (2)
C1b–C6b	1.396 (2)	C2b–C3b	1.394 (2)	C3b–C4b	1.394 (2)	C4b–C5b	1.394 (2)
C5b–C6b	1.391 (2)	C1–C5	3.029 (2)[b]	C2–C8	2.448 (2)[b]	C3–C7	3.067 (2)[b]
Angles deg									
C9–N1–C10	111.0 (1)	C9–N1–C1b	124.1 (1)	C10–N1–C1b	124.8 (1)	N3–N2–C1	122.7 (1)
N3–N2–C9	109.3 (1)	C1–N2–C9	126.8 (1)	N2–N3–C5	125.3 (1)	N2–N3–C10	109.9 (1)
C5–N3–C10	124.7 (1)	N2–C1–C2	113.0 (1)	N2–C1–C8	111.9 (1)	C2–C1–C8	108.0 (1)
C1–C2–C3	123.8 (1)	C2–C3–C4	126.7 (1)	C3–C4–C5	122.8 (1)	C3–C4–C6	119.9 (1)
C5–C4–C6	58.0 (1)	N3–C5–C4	122.3 (1)	N3–C5–C6	123.2 (1)	C4–C5–C6	63.9 (1)
C4–C6–C5	58.1 (1)	C4–C6–C7	120.5 (1)	C5–C6–C7	125.5 (1)	C6–C7–C8	126.6 (1)
C1–C8–C7	122.9 (1)	O1–C9–N1	127.8 (1)	O1–C9–N2	127.2 (1)	N1–C9–N2	104.9 (1)
O2–C10–N1	127.6 (1)	O2–C10–N3	127.6 (1)	N1–C10–N3	104.7 (1)		

[a] Esd's are given in parentheses. [b] Nonbonded distance.

360° with an average angle (α(av)) of 120°, while if nitrogen were tetrahedrally hybridized, α(av) would approach 109.5°.[9] Values of α(av) between 111.6° and 117.9° have been reported for systems in which the adjacent nitrogen atoms of the triazolidinedione ring were bonded to the 1,4 positions of a six-membered ring. However, Kaftory et al.[9] have noted a clear trend toward flattening at nitrogen when a triazolidinedione ring is bonded to the 1,4 positions of progressively larger (five-, six-, or seven-membered) rings.[9b] The completely planar conformation for the triazolidinedione ring has been considered to be the transition state for a simultaneous double nitrogen inversion process.[9a]

Results and Discussion

Homotropilidene Structural Parameters. Bond lengths (Å) and bond angles (deg) for structure **2** were determined by X-ray analysis of crystalline **2** at 293 and 153 K and are shown in Table I. The numbering scheme used for **2** is shown in Figure 2, which is an ORTEP[10] diagram of the 50% probability thermal ellipsoids of the 153 K structure. For comparison purposes, relevant structural parameters of structure **2**, bullvalene ($X = CH{=}CH$), barbaralane ($X = CH_2$), 9-thiabarbaralane dioxide ($X = SO_2$), and semibullvalene (X = bond) are reported in Table II.

The cyclopropyl bond lengths in structure **2** are of primary interest. For crystalline **2** at 153 K the adjacent C4–C5/C5–C6 bond lengths of 1.499 (2) Å are the same as in cyclopropylamine, 1.499 (8) Å,[8a] but shorter than the 1.539 Å of bullvalene in Table II or the 1.513 Å of cyclopropane.[8b] At 293 K, the C4–C5/C5–C6 bond of **2** is a slightly shorter 1.477 (3) Å. The distal bond length in **2** at 153 K is 1.586 (1) Å, which is longer than the 1.512 (3)-Å distal bond in cyclopropylamine,[8a] the 1.539-Å bond of bullvalene, and the 1.513-Å bond of cyclopropane.[8b] At 293 K, the distal bond length in **2** is 1.688 (4) Å;[11,12] however, this long bond is associated with relatively large thermal ellipsoids for C4 and C6.[12]

There are structural similarities between bullvalene and **2** that are worth noting. The C1–C2 (C1–C8) bonds of **2** (1.496 Å at 293 K, 1.513 Å at 153 K) are not appreciably different from those of crystalline bullvalene (1.509 Å).[13] The calculated nonbonded

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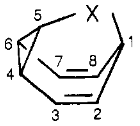
(11) (a) Cyclopropyl bond lengths greater than 1.65 Å, although known, are unusual. For a collection of reported long carbon–carbon single-bond lengths, see: Osawa, E.; Kanematsu, K. In *Studies of Organic Molecules* (*Molecular Structure and Energetics Series*); Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: NY, 1986; Vol. 3, Chapter 7, p 329. (b) Miller, L. S.; Grohman, K.; Dannenberg, J. J.; Todaro, L. *J. Am. Chem. Soc.* **1981**, 103, 6249–6251 and ref 19 therein; 1,5-dimethyl-2,4,6,8-tetrakis(carbomethoxy)-semibullvalene has cyclopropyl bond lengths of 1.782, 1.483, and 1.530 Å. The authors arguably reject a steric explanation for the unusually long bond length. (c) Sellner, I.; Schuster, H.; Sichert, H.; Sauer, J.; Noth, H. *Chem. Ber.* **1983**, *116*, 3751–3761. Cyclopropyl bond lengths of 1.835 and 1.487 Å (average) have been reported for 3,7-dicyano-1,5-dimethylsemibullvalene. A short C4–C6 (C2–C8 in Table II of this paper) distance of 2.048 Å was found. (d) Quast, H.; Christ, J.; Peters, E.-M.; Peters, K.; Schnering, H. G. von *Ibid.* **1985**, *118*, 1154–1175. Cyclopropyl bond lengths of 1.722, 1.502, and 1.481 Å were found for 2,6-dicyano-1,5-dimethylsemibullvalene. (e) See ref 4a. The C2–C8 and C4–C6 internuclear distances are both 1.865 Å for crystalline 2,6-dibromo-3,7-dicyano-1,5-dimethylsemibullvalene. However, this structure is fluxional in the crystalline state.

(12) A referee has suggested that the long distal bond length at 293 K is probably an artifact of thermal disorder (thermal atomic motion), especially in light of the difference between the 293 and 153 K data. A 9-phosphabarbaralane, which exhibits a localized structure in solution, was found by X-ray diffraction to have C4–C6 and C2–C8 distances that were extremely close [1.949 (7) and 2.054 (7) Å]. The thermal ellipsoids at C6 and C8 were noted to be significantly larger than those of the other atoms. Weissman, S. A.; Baxter, S. G.; Arif, A. M.; Cowley, A. H. *J. Am. Chem. Soc.* **1986**, *108*, 529–531.

Table II. Selected Structural Parameters for **2**, Bullvalene, Barbaralane, 9-Thiabarbaralane Dioxide, and Semibullvalene[a]



	2(293 K) crystal	**2**(153 K) crystal	X = CH═CH vapor[b]	X = CH═CH crystal[c]
	Bond Distances, Å			
C4–C5	1.477 (3)	1.499 (2)	1.542 (6)	1.539
C4–C6	1.688 (4)	1.586 (1)	1.542 (6)	1.539
C1–C2	1.496 (4)	1.513 (2)	1.523 (5)	1.509
	Nonbonded Distances, Å			
C2–C8	2.337	2.448	2.515 (11)	
C1–C5	2.999	3.029		3.030[d]
C3–C7	3.026	3.067		
	Bond Angles, Deg			
C2–C1–C8	102.7 (2)	108.0 (1)	111.4	110.2
C4–C5–C6	69.7 (2)	63.9 (1)		60.0

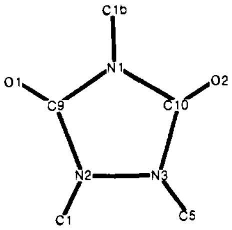
	X = CH_2 MINDO/2[e]	X = SO_2 crystal[f]	X = bond vapor[g]
	Bond Distances, Å		
C4–C5	1.512 (1.492)	1.501 (6)	1.530
C4–C6	1.510 (1.549)	1.561 (6)	1.600
	Nonbonded Distances, Å		
C2–C8	2.327 (2.063)	2.428 (6)	(2.261)
C1–C5			1.485
	Bond Angles, Deg		
C2–C1–C8			(95.2)
C4–C5–C6		62.7 (2)	(63.0)

[a] The numbering has been arbitrarily chosen to facilitate comparisons. Averaged values are given for equivalent bond lengths and bond angles. [b] Andersen, B.; Marstrander, A. *Acta Chem. Scand.* **1971**, *25*, 1271–1276. [c] Amit, A.; Huber, R.; Hoppe, W. *Acta Crystallogr., Sect. B* **1968**, *24*, 865–869. See, also: Johnson, S. M.; McKechnie, J. S.; Lin, B. T.-S.; Paul, I. C. *J. Am. Chem. Soc.* **1967**, *89*, 7123. Luger, P.; Buschmann, J.; McMullan, R. K.; Ruble, J. R.; Matias, P.; Jeffrey, G. A. *Ibid.* **1986**, *108*, 7825–7827. [d] This value was calculated from the atomic coordinates given in Amit et al., ref *c*. This value is 3.067 Å using the data in Luger et al., ref c. [e] Iwamura, H.; Morio, K.; Kunii, T. L. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 841–846. Values in parentheses are from Dewar et al.[7] [f] Christoph, G. G.; Hardwick, S.; Jacobsson, U.; Koh, Y.-B.; Moerck, R.; Paquette, L. A. *Tetrahedron Lett.* **1977**, 1249–1252. [g] Wang, Y. C.; Bauer, S. H. *J. Am. Chem. Soc.* **1972**, *94*, 5651–5657. Values in parentheses are found in: Christoph, G. G.; Beno, M. A. *Ibid.* **1978**, *100*, 3156–3163.

internuclear distance for C2–C8 of **2** at 293 K is 2.337 Å, which at 153 K is lengthened to 2.448 Å. The distance is shorter than the corresponding distance in bullvalene (2.515 Å), but it is longer than that found in semibullvalene (2.261 Å) (Table II). The C1–C5 distances for **2** of 2.999 Å (293 K) or 3.029 Å (153 K) are similar to that for crystalline bullvalene (3.030 Å).

Triazolidinedione Structural Parameters in 2. Important bond lengths (Å) and bond angles (deg) for the triazolidinedione portion of structure **2** at 293 and 153 K are shown in Table III. These values can be compared to extrapolated values for planar triazolidinediones bonded to the 1,4 positions of a six-membered ring. All bond lengths in crystalline **2** at 153 K deviate less than 1% from the extrapolated values for a planar triazolidinedione ring, which has been described as the transition state for a double nitrogen inversion.[9a] Kaftory et al.[9a] have tabulated bond lengths of 27 triazolidinediones, and the N2–N3 bond length of 1.393 Å at 293 K or 1.402 Å at 153 K for **2** is shorter than predicted for bonding of two sp^2-hybridized nitrogen atoms. The C5–N3 bond length in **2** of 1.426 Å at 293 K or 1.430 Å at 153 K is nearly the same as the C–N bond distance of 1.428 Å in cyclopropylamine. This appears to be fortuitous given the structural differences in the two molecules.

Table III. Geometrical Parameters for the Triazolidinedione Portion of Structure **2** and Extrapolated Values[a] for Planar N Atoms[b]



geometrical parameter	triazolidinedione portion[c] 293 K	triazolidinedione portion[c] 153 K	planar nitrogen[c]
	Bond Lengths, Å		
N2–C1	1.458	1.468	1.467
N3–C5	1.426	1.430	
N2–N3	1.393	1.401	1.407
N2–C9	1.352	1.361	1.355
N3–C10	1.350	1.358	
N1–C9	1.394	1.405	1.408
N1–C10	1.397	1.404	
N1–C1b	1.427	1.426	1.435
C9–O1	1.212	1.226	1.217
C10–O2	1.210	1.221	
	Bond Angles, Deg		
C1–N2–N3	122.3	122.7	113.5
C5–N3–N2	124.7	125.3	
C1–N2–C9	126.7	126.8	136.8
C5–N3–C10	125.4	124.7	
N2–N3–C10	109.7	109.9	109.7
N3–N2–C9	109.4	109.3	
N2–C9–O1	127.1	127.2	128.3
N3–C10–O2	127.5	127.6	
N2–C9–N1	105.0	104.9	104.3
N3–C10–N1	104.8	104.7	
N1–C9–O1	127.9	127.8	127.3
N1–C10–O2	127.7	127.6	
C9–N1–C10	110.9	111.0	111.9
C9–N1–C1b	123.9	124.1	124.1
C10–N1–C1b	125.1	124.8	

[a] See ref 9a. [b] The numbering system is arbitrary for **2**. For the symmetrical triazolidinediones there is a degeneracy in the numbering. [c] The average esd for bond lengths or angles in **2** is 0.0025 Å and 0.2° for 293 K data and 0.002 Å and 0.1° for 153 K data. [d] Values are extrapolated from data in ref 9a for 1,4-bridging to a cyclohexane.

Table IV. Calculated Parameters for the Nitrogen Atoms of **2**

vertex	sum of angles, deg 293 K	sum of angles, deg 153 K	α(av),[a] deg 293 K	α(av),[a] deg 153 K	p-character,[b] % 293 K	p-character,[b] % 153 K
N1	359.93	359.96	119.98	119.99	99.95	99.97
N2	358.46	358.84	119.45	119.61	98.95	99.22
N3	359.75	359.93	119.92	119.98	99.83	99.95

[a] α(av) = (sum of the valence angles at N)/3. [b] Reference 14.

The extrapolated bond angle values for planar nitrogen in Table III are for 2,3-diazabicyclo[2.2.2] structures, and, since C1–N2–N3–C5 are parts of a seven-membered ring in **2**, the external angles with N2 and N3 as vertices are not comparable for the two types of systems. However, despite the distortion of the external angles at N2 and N3, the angles of **2** internal to the triazolidinedione deviate by 1° or less from values extrapolated for a planar system.

In Table IV are shown calculations of average angles (α(av)) and percentage of p character for the nitrogen lone-pair orbitals of **2**.[14] Values of α(av) = 120° and p = 100% would be char-

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(13) See ref 5a. Clark, Schleyer, et al. have compared the geometrical effects of cyclopropanes and the corresponding 2-propyl derivatives and have concluded that 2-propyl has greater σ-donating ability than does cyclopropyl. Thus, given the distortion of the cyclopropyl bond lengths in **2**, we might have expected to see a greater bond-shortening effect at C1–C2/C1–C8 than is observed.

Table V. Deviations (Å) of Selected Atoms from the Best Plane C1–C5–C9–C10

atom	dev	atom	dev	atom	dev
		T = 293 K			
C1	+0.0293	C5	−0.0299	C9	−0.0383
C2	+1.2293	C6	−0.8330	C10	+0.0389
C3	+1.5650	C7	−1.4573	N1	+0.0200
C4	+0.8536	C8	−1.1009	N2	−0.0998
				N_3	+0.0104
		T = 153 K			
C1	+0.0181	C5	−0.0185	C9	−0.0237
C2	+1.2811	C6	−0.7703	C10	+0.0242
C3	+1.5891	C7	−1.4742	N1	+0.0201
C4	+0.8147	C8	−1.1618	N2	−0.0911
				N3	−0.0066

acteristic of completely planar nitrogen atoms. Deviations of selected atoms from the best plane C1–C5–C9–C10 of **2** are shown in Table V. At 293 K, atom N3 is 0.01 Å above the best plane, while at 153 K, atom N3 is 0.01 Å below it; atom N2 is 0.10 Å below this plane at 293 K and 0.09 Å below at 153 K. The displacement distances obtained graphically from this information, Δ = 0.045 Å (293 K) and 0.046 Å (153 K) below the plane, can be compared to a Δ value of 0.275 Å for the most planar of the triazolidinediones reported by Kaftory et al.,[9a] where Δ is the distance of the midpoint of the N–N bond from the best plane passing through the carbon atoms bonded to the nitrogen atoms.[15]

Interplay between the Homotropilidene and Triazolidinedione. While a planar geometry has not been attained for a triazolidinedione ring in which the adjacent nitrogen atoms were part of a strained bicyclic system, it has been noted by Kaftory et al.[9] that in diazabicyclo[2.2.*n*] systems the triazolidinedione nitrogens are less tetrahedral and closer to planarity as *n* increases. In structure **2**, a diazabicyclo[3.3.2] system, there are larger bridges and less strain than in the bridged structures studied by Kaftory. Additionally, a planar triazolidinedione ring allows maximum conjugation of N2 and N3 with their adjacent carbonyl groups, thus minimizing lone pair–lone pair repulsion destabilization of the hydrazinyl nitrogens N2 and N3. While geometrical factors in **2** are favorable for a planar triazolidinedione, theoretical considerations suggest that a planar bisected nitrogen atom is the least favorable conformation for an aminocyclopropane,[5a,8a] and maximization of nitrogen electronegativity by sp^2 hybridization should be destabilizing to the cyclopropane.[5a] The counterbalancing factor may be that planarity of the triazolidinedione best minimizes interaction of the N3 lone pair with the cyclopropane by delocalizing these electrons onto the C10 carbonyl.

Cyclopropyl Bond Lengths. The shortened adjacent bonds (C4–C5 and C5–C6) and longer distal bond (C4–C6) in **2** relative to the C–C bonds of cyclopropane[8] are in qualitative agreement with expectations for interaction of a σ-acceptor substituent with the cyclopropane $1e''(L)$ molecular orbital.[5a,8a,16] This is shown in Table VI, which summarizes geometrical predictions for interaction of N3 with various cyclopropyl molecular orbitals. The $1e''(L)$ orbital, which is most affected by substituent electronegativity,[5a] is antibonding at the adjacent cyclopropyl bonds and bonding between the distal carbons.

Table VI. Predicted Geometrical Outcomes for Interaction of N3 with Cyclopropyl Molecular Orbitals in **2**[a]

substituent type	interacting cyclopropane MO[b]	cyclopropyl bond	
		adjacent	distal
σ acceptor	$1e''(L)$	shorter	longer
π donor[c]	$1a'_2$	longer	longer
π donor[d]	$3e'(R)$	(shorter)	(longer)
π donor	$4e'(R)$	longer	longer
π acceptor	$3e'(R)$	longer	shorter

[a] Reference 5a. [b] All interactions except with $1e''(L)$ are of the π type; see ref 5a. [c] See: Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907–2910. [d] MO $3e'(R)$ is occupied.

Rall et al.[8a] have attributed shortening of the adjacent cyclopropyl bond lengths *and absence of an observed bond length change for the distal bond* in aminocyclopropane to a hybridization change at C1, the functionalized carbon. The hybridization change associated with the electronegativity of the nitrogen atom is predicted to be more or less localized and to shorten the adjacent bonds by reducing the p character and increasing the s character at C1. Structural consequences due to dominant σ electron withdrawal from the $1e''(L)$ orbital (Table VI) should have lengthened the distal cyclopropyl bond, which was not observed. In any event, the σ electron withdrawal effect was predicted to be small, because the $1e''(L)$ orbital is primarily CH bonding in character and contributes only π-bonding at the cyclopropyl C–C bonds.

The lengthening of the distal bond of **2**, which accompanies the shortening of the adjacent bonds, suggests a role for the σ-withdrawal mechanism in addition to a hybridization effect. The ring distortions, which are a consequence of the bisected amine conformation (Figure 1), are shown in Table VI to be characteristic of a weak σ-acceptor. The amino group in **2** is distinguishable from that of aminocyclopropane, since the carbonyl group attached to N3 in **2** should increase the σ-acceptor ability of this atom and thus its effect upon cyclopropyl bond lengths.[18]

Durmaz and Kollmar[5b] have made the alternative suggestions that ring strain induced by hybridization changes might be accommodated by simultaneously lengthening the opposite and shortening the adjacent cyclopropyl bonds. However, Rall et al.[8a] have pointed out that the force constants for stretching and compressing C–C bonds are probably too large for such structural changes to relieve bond angle strain. Also, Durmaz and Kollmar[5b] have concluded from calculations of cyclopropylamine and cyclopropylammonium ion that substituent electronegativity does not seem to be an important factor in determining cyclopropyl ring structure. However, Rall et al.[8a] have shown that electronegativity effects had been masked in the calculations by an unpredicted opposing effect.

Some unique, but unidentified, geometric factor associated with the nitrogen atom N3 does not adequately account for the long distal and shorter adjacent cyclopropyl bond lengths in **2**. The geometrical constraint imposed upon the triazolidinedione ring of **2** is not unusual; in fact, the C1–C5 interatomic distance for **2** of 2.999 Å at 293 K and 3.029 Å at 153 K is exceptionally close to the calculated C1–C5 distance of 3.030 Å in bullvalene (Table II). Thus, the geometrical constraint imposed upon the homotropilidene portion of **2** by the C1–C5 nonbonded distance does not require nor account for the observed distortion of the cyclopropyl bond lengths away from the observed values in bullvalene.

NMR Structural Parameters. The ^{13}C and ^1H NMR spectra at 30 °C both clearly show averaged signals for carbons 1 and 5, for carbons 2, 4, 6, and 8, and for the protons attached to these

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(14) (a) Nelsen, S. F.; Cunkle, G. T.; Gannett, P. M.; Ippoliti, J. T.; Qualy, R. J. *Ibid.* **1983**, *105*, 3119–3123. α(av) varies almost linearly with changes in the percentage of p hybridization in the lone pair at nitrogen. (b) Atkins, P. W.; Symons, M. C. R. *The Structure of Inorganic Radicals*; American Elsevier: New York, 1967; Appendix 4. The exact relationship between α(av) and percent p character is given by

$$\%\,p = 100[3(1 - 1/(1 - \cos\alpha(\mathrm{av})))]$$

(15) Burgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065–5067.

(16) See ref 5a for a depiction of Jorgensen–Salem[17] plots of eight cyclopropane MO's using STO-3G wave functions. The orbitals as shown herein are useful to the present discussion.

(17) Jorgensen, W. C.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; pp 153–155.

(18) Interaction of π donors in the bisected conformation (π type)[5a] with the antibonding MO's $1a'_2$ and $4e'(R)$, both of which are antibonding at the adjacent and distal orbitals, should lengthen all of the cyclopropyl bonds of **2**. However, the $1a'_2$ MO is high in energy and the $4e'(R)$ orbital has small coefficients at C1.[5a] A π-type antibonding interaction of the lone-pair electrons of N3 with the bonding MO $3e'(R)$ leads to a prediction in agreement with the observed structural parameters; however, little geometrical change should be observed from this interaction since no net electron transfer should be involved between two filled orbitals.[5a]

carbons. The averaging results from a degenerate Cope rearrangement of the homotropilidene portion of **2**. When the ^{1}H NMR spectrum of **2** was run at lower temperatures, the triplet at δ 4.35 (H2, H4, H6, H8) broadened and began to separate into two widely spaced signals at about −70 °C, beyond which insolubility problems precluded further study.[19]

Conclusion

The longer distal cyclopropyl bond length in crystalline **2** compared to that of cyclopropylamine can be attributed to σ-acceptor effects associated with the electronegativity of the nitrogen atom N3. σ-Acceptor effects and hybridization effects can account for the shorter adjacent bond lengths in **2** relative to cyclopropane. Special geometric constraints associated with bridging of the homotropilidine by the triazolidinedione do not account for the long distal bond lengths in **2**, since the C1–C5 internuclear distance is similar to that of bullvalene. The five bridging carbon atoms connecting N2 and N3 are compatible with the most nearly planar triazolidinedione ring yet observed.

Experimental Section

4-Phenyl-2,4,6-triazatetracyclo[6.3.2.0^{2,6}.0^{7,9}]trideca-10,12-diene-3,5-dione was prepared by the reported procedure.[1] Spectral parameters are as follows: ^{13}C NMR ($CDCl_3$, 30 °C, 25.2 MHz, $CHCl_3$ assigned as 76.91 ppm) δ 73.750 (C1/C5), 40.957 (C2/C4/C6/C8), 127.532 (C6/C9), 131.516, 127.752 (ipso/para C), 128.830, 125.435 (meta/para C), 148.573 (C=O); ^{1}H NMR (CD_2Cl_2, XL 200 MHz, 30 °C, tetramethylsilane) δ 7.49 (Ph), 4.92 (t, J = 7.7 Hz, H1/H5), 4.35 (major coupling t, J = 7.7 Hz, H2/H4/H6/H8), 6.08 (major coupling t, J = 7.7 Hz, H6/H9). At −10 °C the peak at δ 4.35 begins to broaden, at −70 °C it is totally flat, and below this the solute precipitates.

Crystal Structure Data. Intensity data were collected at 293 K and at 153 K on a Nicolet P3 four-circle computer-controlled diffractometer, using graphite-monochromated X-radiation (Cu Kα, λ = 1.5418 Å for 293 K and Mo Kα, λ = 0.71069 Å for 153 K). The crystals are monoclinic, space group $P2_1/c$. The structure was solved by using the 293 K data in the direct methods multiple-solution program MULTAN80.[20] The 293 and 153 K data were used in structure refinements by a full-matrix least-squares procedure[21,22] with anisotropic temperature factors for O, N, and C atoms and isotropic temperature factors for H atoms. The atomic scattering factors used are from a compilation of published values.[24]

293 K data: a = 9.030 (4) Å, b = 16.519 (6) Å, c = 8.681 (5) Å, β = 96.20 (4)°, V = 1287 (1) Å^3, Z = 4, 2059 unique data ($I \geq 2.00\ \sigma(I)$), θ range 0–69.5°, R = 0.060, R_w = 0.063.

153 K data: a = 8.849 (4) Å, b = 16.587 (5) Å, c = 8.643 (5) Å, β = 96.07 (4)°, V = 1261.4 (9) Å^3, Z = 4, 3700 unique data ($I \geq 3.00\ \sigma(I)$), θ range 0–32.5°, R = 0.062, R_w = 0.078.

Acknowledgment. This research was supported by USPHS Grants CA-10925, CA-06927, RR-05539, and CA-22780 from the National Institutes of Health, by Grant BC-242 from the American Cancer Society, and by an appropriation from the Commonwealth of Pennsylvania. We acknowledge Professors P. von R. Schleyer and Edgar F. Kiefer for helpful discussions and Professor J. E. Baldwin for the use of the facilities of Dyson Perrins Laboratory, Oxford University.

Supplementary Material Available: X-ray experimental procedures, ORTEP and stick diagrams, and listings of anisotropic thermal parameters, final atomic parameters, and torsion angles for **2** at T = 293 K and T = 153 K (11 pages); listings of observed and calculated structure factors for **2** at T = 293 K and T = 153 K (41 pages). Ordering information is given on any current masthead page.

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(19) Not all exchange processes that occur in solution are observed in the solid state. Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 7396–7397. Macho, V.; Miller, R. D.; Yannoni, C. S. *Ibid.* **1983**, *105*, 3735–3737. Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208–216. For a semibullvalene that is fluctional in the crystalline state, see ref 4a and 11e. Note, also: Kobayashi, Y.; Ando, A.; Kawada, I.; Kumandaki, I. *J. Am. Chem. Soc.* **1981**, *103*, 3958–3959.

(20) Main, P. *Multan80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York: York, England, 1979.

(21) Carrell, H. L. *ICRFMLS. Modification of UCLALS4*; Institute for Cancer Research: Philadelphia, 1975.

(22) Gantzel, P. K.; Sparks, R. A.; Long, R. E.; Trueblood, K. N. *UCLAS4. Full-Matrix Least-Squares Program in FORTRAN IV*, 1969.

(23) $R = \sum||F_o| - |F_c||/\sum|F_0|$, where F_o is an observed structure factor and F_c is a structure factor calculated from a postulated structure. R is a measure of the extent to which the measured x-ray diffraction pattern of a structure agrees with that calculated from the parameters of the structure determined by analysis of the diffraction data. $R_w = (\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2)^{1/2}$ is another measure of this agreement incorporating the weight, w, of each observation. R_{obsd} is the agreement using those data considered to be "observed." R_{all} is the agreement using all data measured.

(24) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71–102.

Dynamic Behavior of Dicobalt Hexacarbonyl Propargyl Cations and Their Reactions with Chiral Nucleophiles

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Abstract: The dynamic behavior of several dicobalt hexacarbonyl propargyl cations has been investigated by variable temperature ^{1}H and ^{13}C NMR methods. Two distinct fluxional properties have been identified. The temperature-dependent NMR spectra of these cations are consistent with a lower energy antarafacial migration of an alkylidene ligand from one cobalt tricarbonyl unit to the other. This motion results in the enantiomerization of the cation. A diastereomerization process has been detected at elevated temperatures. The relevance of this fluxional behavior to the stereochemical outcome of cation alkylation reactions is discussed. For example, on treatment with a chiral, nonracemic nucleophile (Evans' boron enolate) an unusual double stereodifferentiating reaction is found to occur. The yield and stereochemistry of the reaction suggest the intermediacy of a cation that (1) racemizes at a rate that is fast relative to alkylation and (2) reacts with different rates (kinetic resolution) with the chiral nucleophile. A stereochemical model is proposed that accounts for these results and allows predictions to be made concerning the outcome of other nucleophile–electrophile combinations.

Transition-metal complexes of alkynes, as transient reaction intermediates and isolable compounds, have played a prominent role in the chemistry of acetylenes. Mononuclear[1] and dinuclear[2] complexation results in marked changes in alkyne structure and

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