fied with dilute fluoroboric acid, diluted with acetone, poured into H_2O, and extracted thoroughly with ether. The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give an orange oil (0.022 g) whose nmr spectrum indicated the presence of 1-methyl-1-phenyl-2-thio-3-chromene (19) (~48%), 1-phenyl-2-thio-3-chromene (14b) (~7%), and unknown material (~45%). The products were not separated. No attempt was made to reisolate the 15b regenerated upon acidification from the aqueous extracts.

The decomposition of 1-phenyl-2-methyl-2-thianaphthalene (16) was studied on a preparative scale. Into a solution of potassium tert-butoxide (0.216 g, 0.00193 mol) in 30 ml of DMSO under N_2 was injected 1-phenyl-2-methyl-2-thio-3-chromenium tetrafluoroborate (15b) (0.629 g, 0.00193 mol) dissolved in 10 ml of DMSO. The solution immediately turned deep red. The reaction mixture was stirred at 40° for 4 hr during which the color of the mixture had faded to a yellow-orange. It was poured into H_2O and extracted with ether, and the extracts were washed thoroughly with H_2O. The extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give 0.440 g of a brown oil. Chromatography on neutral alumina (Woelm, activity 1) (4:1 petroleum ether–benzene) gave 0.217 g of essentially pure 1-methyl-1-phenyl-2-thio-3-chromene (19): nmr (CCl_4) δ 1.90 (s, 3), 6.15 (d, 1, J = 10 Hz), 6.55 (d, 1, J = 10 Hz), and 6.7–7.7 (m, 9); mass spectrum (70 eV) m/e (rel intensity) 238 $(M^+, 100)$, 239 $(M^+ + 1, 18.8)$, 240 $(M^+ + 2, 5.75)$, calcd for $C_{16}H_{14}S$ $(M^+ + 1, 18.3)$ and $(M^+ + 2, 5.8)$. Further elution with 50% benzene–ether gave 0.169 g of an orange oil showing absorption signals assignable to 1-phenyl-2-thio-3-chromene (14b) (25%) and multiple absorptions from 0.70 to 2.4 and 6.6 to 7.8 ppm (75%), the origin of which was indeterminate.

Generation of 1-(p-Chlorophenyl)-2-methyl-2-thianaphthalene (17). A solution of 1-(p-chlorophenyl)-2-methyl-2-thio-3-chromenium perchlorate (15c) (0.073 g, 0.000196 mol) was dissolved in 0.20 ml of DMSO-d_6 and injected into a suspension of potassium tert-butoxide (0.022 g, 0.000196 mol) in DMSO-d_6 under a N_2 atmosphere in an nmr tube according to the general procedure. A deep red solution was produced whose nmr spectrum (obtained within 3 min of generation) exhibited signals attributable to 17: δ 1.85 (s, 3), 5.75 (d, 1, J = 8 Hz), 6.5–7.60 (m, 15), and 7.65 (d, 1, J = 8 Hz). Several experiments in which 17 was generated by the same general procedure gave 17 in amounts ranging from 50 to 54% based on comparison of the integration of the signals at 1.85, 5.75, and 6.5–7.60 ppm. Acidification of the solution in the nmr tube after 5 min in the nmr probe with dilute $HClO_4$ regenerated the spectrum of the starting salt, 15c, in approximately 50% yield, although the material was not reisolated.

When 17 was generated at room temperature and maintained at 40° in the nmr probe, new peaks began to appear after a few minutes. The intensity of the doublet at 5.75 ppm began to decrease and the multiplet from 6.8 to 7.7 ppm began to show more peaks in the region 6.5–7.0 ppm. The general appearance of the phenyl region changed while a singlet began to appear at 1.90 ppm at the expense of the singlet at 1.85 ppm. After 15 min, 50% of 17 had been converted to another product, based on integration of the doublet at 5.75, the singlet at 1.87, and the emerging singlet at 1.90 ppm.

The generation and observation of 17 were also performed at a temperature of 20–22°. Thianaphthalene, 17, was initially generated in the same 50–54% yields as outlined above. However, the lowered temperature prevented any noticeable decomposition from occurring for as long as 90 min.

Determination of the Decomposition Products of 1-(p-Chlorophenyl-2-methyl-2-thianaphthalene (17). Into a suspension of potassium tert-butoxide (0.061 g, 0.00055 mol) in 15 ml of DMSO (stirred under a nitrogen atmosphere) was injected 1-(p-chlorophenyl)-2-methyl-2-thio-3-chromenium perchlorate (15c) (0.200 g, 0.00054 mol) dissolved in 1.0 ml of DMSO. The solution turned cherry red and was maintained at 37–40° for 24 hr. After that time, the solution had faded to a yellow-orange. The reaction mixture was poured into H_2O and extracted thoroughly with ether, and the extracts were washed thoroughly with water. The extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give an orange oil (0.142 g, 85%). Chromatography on neutral alumina (Woelm, activity grade 1), eluting first with petroleum ether mixtures containing up to 50% benzene, gave 0.058 g of a pale yellow oil, identified by its spectral characteristics as 1-(p-chlorophenyl)-1-methyl-2-thio-3-chromene (18): nmr (CCl_4) δ 1.90 (s, 3), 6.20 (d, 1, J = 10 Hz), 6.62 (d, 1, J = 10 Hz), and 6.9–7.4 (m, 8); mass spectrum (70 eV) m/e (rel intensity) 272 $(M^+, 100)$, 273 $(M^+ + 1, 19)$, and 274 $(M^+ + 2, 39)$. Further elution with 50% benzene–ether gave 0.081 g of an orange oil whose nmr spectrum indicated that it was approximately 30% 1-(p-chlorophenyl)-2-thio-3-chromene (14c), identified by comparison of the nmr spectrum with that of authentic 14c; nmr (CCl_4) δ 5.0 (s), 6.2 (d), and 6.7–7.6 (m), also 0.90–2.4 (m), 5.6–6.6 (m), and 6.7–7.8 (m).

Structure of a Hydrazino-Bridged [12]Annulene. A 12π Monocyclic Antiaromatic Compound

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Contribution from the Department of Chemistry, The University of Alabama, University, Alabama 35486. Received January 18, 1974

Abstract: The crystal structure of 8b,8c-diazacyclopent[fg]acenaphthylene has been determined from three-dimensional X-ray data measured by counter methods. The compound crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions a = 7.643 (4), b = 4.138 (3), c = 13.452 (6) Å, β = 90.38 (5)°, and ρ_{calcd} = 1.41 g/cm^3 for Z = 2. Least-squares refinement gave a conventional R factor of 0.076 for 349 unique observed reflections. The molecular framework of this hydrazino-bridged [12]annulene is planar to within 0.02 Å. This fact, and the presence of a nitrogen–nitrogen single bond, establish its structure. The X-ray and pmr data establish that this compound is a planar 12-π-monocyclic antiaromatic compound.

An understanding of the net energy changes associated with π-electron delocalizations remains one of the basic questions in organic chemistry. Molecular orbital theory predicts[1] that π-electron delocalization

(1) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

may have one of three possible effects on the net energy of the system: it may increase, decrease, or have no effect on that energy. The $4n + 2$ monocyclic systems, aromatic compounds, represent an experimental verification of those instances where an energy decrease accompanies π-electron delocalizations. The

[4.4.2]propellapentaenes[2] and barrelene,[3] on the other hand, may well represent examples of π systems where delocalization causes no net change in the energy of the compounds. Finally, planar $4n$ π-monocyclic systems can potentially represent instances of π-delocalized compounds where the π-delocalization causes an increase in the energy of the system. These types of systems have been defined by Dewar[4] and Breslow[5] as *antiaromatic*. Interestingly, it has recently been shown that both the aromatic as well as antiaromatic systems will tend toward nonaromatic behavior as the ring sizes increase.[6] Thus, in going from a 6π system to a 30π system, in increments of 4π electrons, it has been predicted that there will be a decrease in the resonance energy from 0.4345 to 0.1549 eV, while in going from the antiaromatic 4π to the 28π systems in increments of 4π electrons, the resonance energy is predicted to increase from −1.05 to −0.0578 eV. Thus, as these antiaromatic rings become larger, their properties are expected to approach those of nonaromatic compounds. Experimental verification of antiaromaticity has so far been largely hampered by the fact that the known neutral $4n$ monocyclic π systems are neither planar nor rigid. Trost and coworkers have recently prepared pyracylenes (1) which are described as perturbed [12]-annulenes.[7]

1
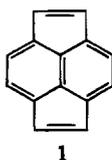
This ring system can be looked at as a model for a planar [12]annulene where the central double bond has only a minimal effect upon the π-electronic periphery of the ring system. It has been suggested that the abnormal deshielding effect of the ring protons in going from a dihydropyracyclene to pyracylene (Δ 1.00 ppm) may well be caused by the presence of a paramagnetic ring current in pyracylene when it is placed into a magnetic field.

Some time ago we reported the synthesis of 8b,8c-diazacyclopent[fg]acenaphthylene, a hydrazino-bridged [12]annulene (6a and/or 6b).[8] This compound potentially represents an excellent model for a planar [12]-annulene. As commented on in our earlier communication, this compound could also exist in valence-bond tautomeric equilibrium with the conceivably aromatic [1,6]diazadecapentaene derivative 7. The latter structure might, however, suffer from nitrogen–nitrogen lone pair repulsions of sufficient strength to counteract any resonance stabilization expected to be present in the 10π-electron central ring.

In order to establish the correct structure of this compound, at least in the solid state, we obtained its con-

figuration from an X-ray crystallographic analysis, and now wish to describe the results of this study.

Synthesis. Scheme I delineates the reactions which have led to the formation of 8b,8c-diazacyclopent[fg]-acenaphthylene (6) and its structural interrelationship with the starting compound 3,4,7,8-tetrahydro-8b,8c-diazacyclopent[fg]acenaphthylene. While the formation of compound 3 from 2 is a low-yield (25%) reaction, the treatment of the tetraketone 4 with hydrazine affords compound 3 in 80% yield, and consequently constitutes the route of choice for the synthesis of compound 3. Table I lists the pmr parameters for com-

Table I. Pmr Spectral Parameters of 8b,8c-Diazacyclopent[fg]acenaphthylene and Derivatives

Compd[a,b]	—————Chemical shifts (τ)—————			
	H_1, H_6	H_2, H_5	H_3, H_4	H_7, H_8
3	4.15	4.15	7.04	7.04
5	3.68	3.68	6.72	3.18
6	4.87	4.87	4.78	4.78

[a] Dilute solutions in $CDCl_3$. [b] Numbers are as found in text.

pounds **3**, **5**, and **6**. These data, in conjunction with the arguments presented in our earlier communication, constitute the necessary structure proofs for these substances.

Scheme I
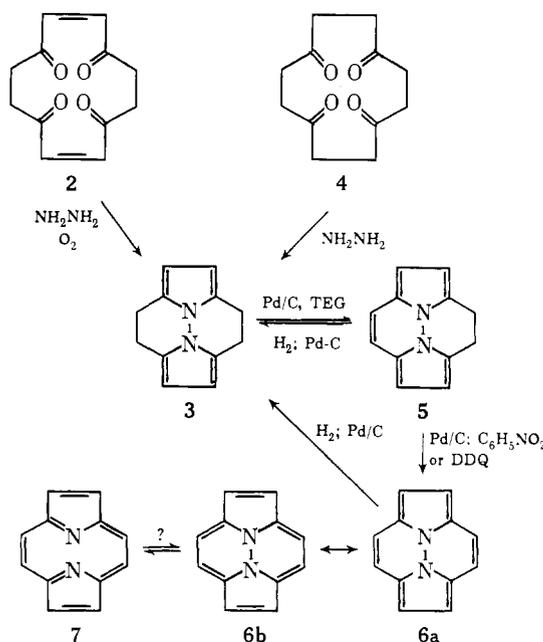
Results and Discussion

The X-ray crystallographically determined dimensions for compound 6 are given in Figure 1 and Table II. Clearly, the most striking and fascinating feature is the planarity of the compound: none of the 12 carbon atoms deviates by more than 0.02 Å from the least-squares plane of the molecule.[20] As anticipated for structure **6**, the observed N–N bond distance, 1.37 (1) Å, is typical of that predicted (1.362 Å) and found (1.380 Å) in molecules containing an N–N bond. These results clearly established that we are dealing with structure **6**, and not its aromatic valence-bond tautomer **7**. Examination of the various peripheral C–C bond

(2) L. A. Paquette and J. C. Phillips, *J. Amer. Chem. Soc.*, **91**, 3973 (1969).

(3) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 2330 (1969).

(4) M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 121 (1965).

(5) R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

(6) H. P. Figeys, *Tetrahedron*, **26**, 5225 (1970).

(7) B. M. Trost, G. M. Bright, C. Frihart, and D. Brittelli, *J. Amer. Chem. Soc.*, **93**, 737 (1971).

(8) W. W. Paudler and E. A. Stephan, *J. Amer. Chem. Soc.*, **92**, 4468 (1970).

Figure 1. Molecular structure of 8b,8c-diazacyclopent[*fg*]acenaphthylene with the atoms displayed as 50% probability ellipsoids for thermal motion. The standard deviations in the bond lengths are less than 0.01 Å, and in the bond angles, 0.3°

Table II. Crystal Data

Mol formula: $N_2C_{12}H_8$
Mol wt: 180.2
Linear abs coeff μ: 6.73 cm^{-1}
Max crystal dimensions: 0.062 × 0.15 × 0.72 mm
Space group: monoclinic, $P2_1/n$
Molecules/unit cell: 2
Cell constants:^{a} a = 7.643 (4), b = 4.138 (3), c = 13.452 (6) Å,
 β = 90.38 (5)°
Cell vol: 425 Å^3

^{a} Cu Kα radiation, λ 1.54051 Å. Ambient temperature of 23 ± 1°

lengths in compound **6** reveals that all of these bonds are within ±0.03 Å of 1.39 A. If the compound were constituted like a typical polyene, the bond length would be expected[1] to alternate approximately between 1.35 and 1.47 Å; however, this is clearly not the case, and, consequently, we are dealing with a compound whose π-electronic periphery is considerably delocalized. In terms of the resonance theory notation, the compound should, consequently, be described as composed of the nonaromatic canonical structures **6a** and **6b**, or by notation **6c**. Thus, 8b,8c-diazacyclo-

6c
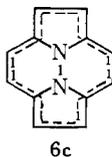
pent[*fg*]acenaphthylene (**6**) is an example of a planar 12π-monocyclic system which, based upon Dewar's and Breslow's concepts, may be antiaromatic. This antiaromaticity should be reflected in the existence of a paramagnetic ring current in the compound, when it is placed into a magnetic field. One can examine this question by comparing the pmr spectra of compounds **5** and **6**. The former substance has an aromatic 14π-electronic ring system which, by dehydrogenation, is

converted to the potentially antiaromatic compound **6**. The pyrrole ring protons in compound **6** become more shielded by 1.19 ppm, while the other olefinic protons experience a shielding of 1.6 ppm in going from **5** to **6**. This dramatic shielding effect, caused by introduction of the additional double bond, can be interpreted as being the result of any one or a combination of the following three factors: an increase of the electron density at the carbon atoms, a destruction of the diamagnetic ring current, and/or the presence of a paramagnetic ring current. It is certainly to be expected that the diamagnetic current will no longer be present in compound **6**. An increase in the electron densities caused by the central nitrogen atoms would not be expected to be very significant, especially in view of the quantum chemical calculations done by Trost,[7] which have shown that there is a very small, if any, contribution to the periphery by the central carbon atoms in pyracyclene (**1**). The major factor for the shielding effects in going from compound **5** to compound **6** is, in all probability, due to the ability of compound **6** to maintain a paramagnetic ring current. If one takes the chemical shift of the "internal" olefinic hydrogens in the bond alternating nonplanar cyclooctatriene as standard (τ 4.3), then the chemical shifts of the hydrogens at τ 4.87 and 4.78, respectively, probably reflect the approximate paramagnetic ring current contribution to the proton chemical shifts of compound **6** (0.47 and 0.48 ppm respectively for the pyrrolic and olefinic protons). Thus, it appears that compound **6** represents an example of a planar rigid 4n (n = 3) system which can maintain a paramagnetic ring current.

A comparison of the proton chemical shifts of compound **6** with those of cycl[3.3.3]azine (**8**) suggests that

8
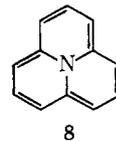
there exists a much larger paramagnetic ring current in this modified 4n (n = 3) annulene than in the hydrazine bridged one **6**. The maximum paramagnetic ring current for this type of annulene would be expected to be observed in the hypothetical all cis-bonded, planar and rigid compound.[9] This ring current is expected to decrease as the [12]annulene structure deviates from this "ideal" case by an increasing number of trans double bonds. Since the cycl[3.3.3]azine (**8**) has a cis–trans–cis–trans–cis–trans alternating bonding, while the hydrazine bridged annulene **6** has a cis–trans–trans–cis–trans–trans structure, the latter compound deviates considerably more from the "ideal" case, and as such should be able to maintain a smaller paramagnetic ring current than compound **8**. Consequently, on a qualitative basis, these superficially amazing differences in chemical shifts can be readily rationalized. We are in the process of preparing other 4n hydrazine-bridged annulenes with the hope of expanding our understanding of these interesting compounds.

Experimental Section

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The mass spectra

(9) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966).

Table III. Final Fractional Coordinates and Anisotropic Thermal Parameters[a]

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	0.5441 (5)	0.0960 (13)	−0.0330 (3)	171 (10)	444 (39)	50 (3)	−4 (15)	15 (4)	−19 (9)
C (1)	0.4624 (7)	0.2023 (16)	−0.1192 (4)	199 (13)	434 (53)	46 (3)	53 (19)	−4 (5)	−19 (10)
C (2)	0.5952 (9)	0.3673 (18)	−0.1645 (4)	268 (14)	646 (59)	57 (3)	−9 (25)	21 (6)	−14 (13)
C (3)	0.7478 (8)	0.3646 (19)	−0.1069 (4)	224 (14)	637 (61)	69 (4)	−54 (23)	36 (6)	−30 (13)
C (4)	0.7097 (7)	0.1713 (17)	−0.0215 (4)	165 (12)	567 (54)	54 (3)	54 (20)	6 (5)	−28 (11)
C (5)	0.8006 (8)	0.0699 (18)	0.0670 (4)	251 (15)	491 (56)	68 (4)	25 (23)	−4 (7)	−44 (12)
C (6)	0.2882 (8)	0.1233 (18)	−0.1344 (4)	252 (14)	631 (57)	50 (3)	86 (24)	2 (6)	−21 (13)
H (3)	0.5830[b]	0.4789	−0.2279						
H (4)	0.8578	0.4711	−0.1193						
H (5)	0.9218	0.1305	0.0789						
H (6)	0.2276	0.2001	−0.1935						

[a] Anisotropic thermal parameters $\times 10^4$ defined by $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Hydrogen atoms are in calculated positions which were not refined. All hydrogen atoms were assigned an isotropic temperature factor of 5.0.

were obtained with a Hitachi Perkin-Elmer RMU-6M mass spectrometer. The pmr spectra were recorded on a Varian HA-100 spectrometer. Elemental analyses were determined in the analytical services laboratory of this department. Thin-layer chromatography was done using silica gel G plates, visualization being accomplished by immersion in an iodine vapor bath.

3,4,7,8-Tetrahydro-8b,8c-diazacyclopent[fg]acenaphthylene (3). Method A. 1,1′,2,2′-Tetramethoxytetrahydro-5,5′-ethylene-1,2-di-(2-furyl)ethane[8] (5 g) was added to 100 ml of 0.1 N sulfuric acid at 0–5°. After stirring for 1 hr at 5° the almost-clear solution was filtered by suction. The filtrate was neutralized by addition of solid sodium carbonate, and an excess of cooled hydrazine hydrate (85%, 5 ml) was then added with vigorous stirring to the cold filtrate at such a rate that the temperature never exceeded 10°. Stirring was continued for 4 hr at 10°. The light yellow precipitate which formed was filtered by suction and dried in vacuo. Sublimation at 120° (0.4 Torr) yielded 0.74 g (25%) of white crystals, mp 172–173°; mol wt (mass spectrometric) 184. Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.20. Found: C, 78.25; H, 6.71; N, 15.34. The pmr spectrum of this compound exhibits two singlets at τ 4.15 (4 H) and τ 7.04 (8 H); uv (ethanol) λ_{max} mμ (log ϵ) 212 (4.24), 251 sh (3.91), 258 (3.97), 265 sh (3.84); λ_{min} 238 mμ (log ϵ 3.77).

Method B. To a solution of 120 mg (0.0005 mol) of the tetraketone 4 in 3 ml of glacial acetic acid maintained at 80° and under a N_2 atmosphere was added, dropwise and with stirring, 1.0 ml (0.014 mol) of 85% hydrazine hydrate. The reaction mixture was heated for 10 min and then made basic with Na_2CO_3 solution and extracted with 3 × 25 ml of $CHCl_3$. The $CHCl_3$ solution was washed with 10 ml of H_2O and with saturated NaCl solution, and the organic layer was finally dried over anhydrous Na_2CO_3. The solvent was evaporated and a light brown solid was obtained, which upon sublimation (120° (0.4 Torr)) gives 70 mg (75% yield) of compound 3.

3,4-Dihydro-8b,8c-diazacyclopent[fg]acenaphthylene (5). A mixture of 100 mg of compound 3 and 100 mg of Pd/C (10%) in 10 ml of triethylene glycol was refluxed under a nitrogen atmosphere for 4 hr, cooled, and filtered by suction. After the addition of 50 ml of distilled water, the filtrate was extracted with diethyl ether (3 × 50 ml). The combined ether extracts were dried over solid sodium carbonate (anhydrous); after evaporation of the solvent, the residue was chromatographed on neutral alumina, activity grade 11 (Brockmann). Elution with hexane yielded an off-white solid. Rechromatography followed by sublimation at 70° (0.4 Torr) and recrystallization of the sublimate from hexane yielded 28 mg of white crystals, mp 168–170°: mass spectrometric molecular weight, 182; cf. Table I for pmr data; uv (ethanol) λ_{max} mμ (log ϵ) 214 (3.4), 240 (4.27), 245 sh (4.26), 316 sh (3.29), 332 sh (3.58), 344 (3.72), 362 (3.00); λ_{min} mμ (log ϵ) 220 (3.26), 195 (1.84), 354 (3.60). Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.13; H, 5.49; N, 15.38. Found: C, 79.16; H, 5.55; N, 15.73.

Reduction of 3,4-Dihydro-8b,8c-diazacyclopent[fg]acenaphthylene. A solution of 5 mg of compound 5 in 20 ml of ethanol was hydrogenated at atmospheric pressure in the presence of Pd/C (10%) as catalyst. After the calculated quantity of hydrogen needed to reduce one double bond was absorbed, no further reduction took place. After filtration, the colorless solution exhibited the uv spectrum of compound 3. Thin layer chromatography (benzene–hexane, 1 : 4) showed only one spot, identical in R_f value with compound 3.

8b,8c-Diazacyclopent[fg]acenaphthylene (6). To a boiling solution of 100 mg of compound 3 in 50 ml of toluene (under a nitrogen
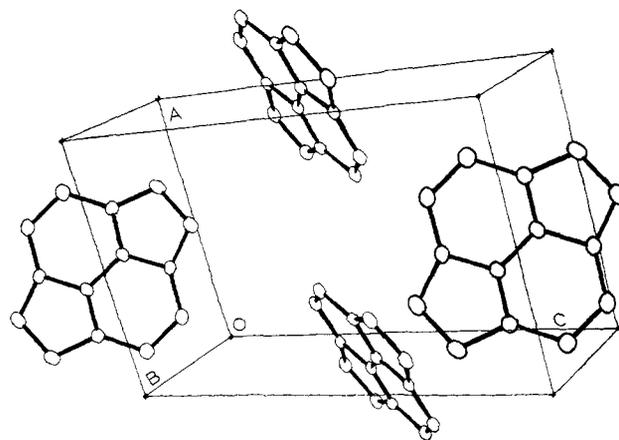
Figure 2. The crystal packing of four molecules of 8b,8c-diazacyclopent[fg]acenaphthylene with a superimposed unit cell.

atmosphere) was added dropwise over a period of 30 min a solution of about 200 mg of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) in 20 ml of toluene. The solution was refluxed for an additional 2 hr, and the cooled reaction mixture was filtered by suction. The black residue was washed twice with 25 ml each of methanol, and the purple filtrate was evaporated in vacuo. Chromatography of the crude material in hexane on neutral alumina (activity grade 11 (Brockmann)) produced very dark purple, almost black crystals. The use of compound 5 as starting material led to the same results. Sublimation of the crude product at 80° (0.4 Torr) yielded 30 mg (30%) of the purple compound 3, mp 143–145°; cf. Table I for pmr data; uv–visible spectrum $\lambda_{max}^{ethanol}$ mμ (log ϵ) 227 (4.36), 250 sh (4.01), 260 sh (3.59), 297 sh (3.71), 312 (3.95), 325 (3.92), 470 sh (1.45), 498 (1.59), 537 (1.64), 586 (1.53), 643 (1.14); $\lambda_{min}^{ethanol}$ mμ (log ϵ) 237 (4.06), 275 (0), 317 (3.81), 520 (1.40), 623 (1.01): mol wt (mass spectrometric), 180. Anal. Calcd for $C_{12}H_8N_2$: C, 80.07; H, 4.48; N, 15.56. Found: C, 79.84; H, 4.60; N, 15.29.

Catalytic hydrogenation under the same conditions as described for the reduction of 5 gave the same results.

X-Ray Data Collection. Final lattice parameters as determined from a least-squares refinement of the angular settings of 12 reflections accurately centered on an ENRAFNONIUS CAD-4 diffractometer are given in Table III. Data were taken on the diffractometer with graphite crystal monochromated copper radiation. The crystal was aligned such that no symmetry axis was coincident with the ϕ axis of the diffractometer. The diffracted intensities were collected by the ω–2θ scan technique with a take-off angle of 3.5°. The scan rate was variable and was determined by a fast 20° min⁻¹ prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.3° min⁻¹. Moving-crystal, moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where $A = 0.62°$ and $B = 0.35°$. Aperture settings were deter-

mined in a like manner with $A = 4$ mm and $B = 4$ mm. Other diffractometer parameters and the method of estimation of standard deviations have been described previously.[10] As a check on the stability of the instrument and the crystal, two reflections, the (200) and (002), were measured after every 30 reflections; no significant variation was noted.

One independent quadrant of data was measured out to $2\theta = 110°$; a total of 349 unique reflections ($I > 2\sigma(I)$) was obtained. The intensities were corrected for Lorentz and polarization effects but not for absorption, since the extreme values of the transmission factors were 0.90 and 0.95.

Fourier calculations were made with the ALFF[11] program. The full-matrix least-squares refinement was carried out using the Busing and Levy program ORFLS.[12] The function $w(|F_o| - |F_c|)[13]$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from the compilations of Cromer and Waber[14] for C and N; those for hydrogen were from "International Tables for X-ray Crystallography."[15] Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE program.[16] Crystal structure illustrations were obtained with the program ORTEP.[17]

(10) J. L. Atwood and K. D. Smith, *J. Amer. Chem. Soc.*, **96**, 994 (1974).

(11) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, USAEC Report IS-2625, Ames Laboratory, Iowa State University, Ames, Iowa, 1971.

(12) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(13) J. M. Robertson and J. G. White, *J. Chem. Soc.*, 358 (1947).

(14) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(15) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(16) W. K. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(17) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794,

Structure Solution and Refinement. The structure was solved by the straightforward application of the direct methods program MULTAN.[18] Anisotropic refinement of the seven nonhydrogen atoms in the asymmetric unit with $1/\sigma^2$ weights gave agreement indices of 0.102 and 0.099. Inclusion of hydrogen atom contributions at calculated positions (C–H bond length assumed to be 0.95

$$R_1 = \sum |F_o| - |F_c|/\sum |F_o|$$

$$R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$$

Å) and further anisotropic refinement of the nonhydrogen atoms led to final values of $R_1 = 0.076$ and $R_2 = 0.073$. Unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. A final-difference Fourier map showed no feature greater than 0.2 e/Å^3. The final values of the positional and thermal parameters are given in the microfilm edition.[19,20]

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6132.

Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965, p 70.

(18) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, *Sect. A*, **27**, 368 (1971).

(19) See paragraph at end of paper regarding supplementary material.

(20) The equation of the plane is $0.2830X - 0.8300Y - 0.4806Z - 1.0825 = 0$.

Studies Concerning Complexes of Ozone with Carbon π Systems

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Abstract: The formation and characterization of the first π complexes observed between ozone and aromatic or olefinic π systems are described. A correlation was made between the ionization potentials of a group of aromatic substrates and the wavelength of the absorption of their ozone complexes in the visible region. Two of the complexes were allowed to react with certain cis and trans olefins. The cis–trans ratios of the ozonides produced were different from those of the ozonides obtained by ozone alone in the cases of the *cis*- and *trans*-1,2-diisopropylethylenes. However, there was no appreciable difference in the results obtained using complexed or uncomplexed ozone with the less bulky *cis*- and *trans*-3-hexenes.

In previous communications[1,2] the formation of π complexes between ozone and 1-mesityl-1-phenylethylene, 1-mesityl-1-phenylethane, 1-methoxyl-1,2,2-trimesitylethylene, and mesitylene was reported. The present paper gives additional experimental details concerning the complexes already reported and extends the work to several new complexes, elucidation of their

(1) P. S. Bailey, J. W. Ward, and R. E. Hornish, *J. Amer. Chem. Soc.*, **93**, 3552 (1971).

(2) P. S. Bailey, J. W. Ward, R. E. Hornish, and F. E. Potts, III, *Advan. Chem. Ser.*, No. 112, 1 (1972).

structures, and to ozonations of cis and trans olefins using two of the complexes as ozonating agents.

The discovery of the first complex ever observed between ozone and a carbon π system (that of 1-mesityl-1-phenylethylene)[1,2] resulted from a search for a possible precursor to the epoxide which is the major product of ozonation of 1-mesityl-1-phenylethylene at ordinary temperatures.[2,3] Ozonation of the olefin (with ozone–nitrogen) at $-120°$ still resulted in the

(3) P. S. Bailey and A. G. Lane, *J. Amer. Chem. Soc.*, **89**, 4473 (1967).