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Steric and Conjugational Electronic Effects on the Configuration of Acylated Hydrazines

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Abstract: The crystal structures of twelve N,N′-acylated cyclic hydrazines are described. In five adducts of 1,2,4-triazolidine-3,5-dione with various cyclopentadiene derivatives, it is shown that the configuration of the triazolidinedione moiety with respect to the bicycloheptyl rings is highly sensitive to very small differences in steric effects. The degree of flattening of the N atoms at the N–N bond is determined by the steric repulsions of the substituents. The average valence angle (α_{av}) at the nitrogens ranges between 110.5 and 112.0°. Increasing the size of N,N′ rings and replacing the urea-type nitrogen of the triazolinedione ring by carbon is shown to cause significant flattening at the hydrazine nitrogens, and five of the other seven structures described here are nearly flat at nitrogen (α_{av} greater than 119°).

The transition state for nitrogen inversion is achieved when the nitrogen atom becomes planar. In acyclic hydrazines, conformations with the lone pairs at nitrogen perpendicular are electronically favored, and the nitrogens invert one at a time, with a substantial increase in nitrogen inversion barrier when the noninverting nitrogen lone pair orbital is forced to be coplanar with that of the inverting nitrogen.[1] When acyl groups or other mesomerically electron-withdrawing groups are attached to the nitrogens of an acyclic hydrazine, the nitrogens flatten substantially, and the nitrogen inversion barrier is too low to measure by NMR.[2] When the nitrogens of an *N,N′*-diacylhydrazine are linked by cyclic alkyl groups, however, the nitrogen lone pairs are forced to assume angles far from 90°, and there is significant lone pair–lone pair interaction, resulting in substantially pyramidal acylated nitrogen atoms.[3] Hydrazines linked N,N′ by two rings small enough to hold the CN,N′C angles in both rings near 0° may well be required to flatten both nitrogens at once to accomplish nitrogen inversion. The crystal structures of a set of compounds containing the 1,2,4-triazolidine-3,5-dione ring fused to a bicyclic ring system show that in most of them, the hydrazine nitrogens adopt significantly pyramidal configurations,[4] despite the presence of an acyl group on each nitrogen and absence of the steric inhibition to resonance which occurs when the nitrogens of 2,3-diazabicyclic hydrazines are acylated by reagents which do not link the acyl groups in a small ring.[3] Each carbonyl group of the triazolidinedione ring is conjugated to N4 as well as to one of the hydrazine nitrogens, which should lead to a decrease in the resonance interaction of the hydrazine nitrogen with the carbonyl group attached to it compared to that of an alkylated carbonyl group, presumably causing more facile bending at the hydrazine nitrogen. The lack of molecules having planar hydrazine nitrogens in the triazolidinedione series previously studied[4] prevented examination of extrapolated geometrical parameters near the transition state for double nitrogen inversion. We were therefore prompted to study the structural features necessary to achieve flattening at the nitrogen of hydrazines in which the nitrogen lone pairs are held near coplanarity. Two possible ways to induce flattening, increasing the steric hindrance in bent structures and substituting the N4 group, are discussed.

A. Steric Effects on the Configuration of the Adducts 1,2,4-Triazolidine-3,5-dione with Various Cyclopentadiene Derivatives. Molecular Structure and Discussion. Schematic drawings with atom numbering[5] and stereoscopic drawings down the N–N hydrazine bond are shown in I–V and Figures 1–5, respectively. Comparisons of bond lengths and angles are given in Tables I and II. The corresponding atomic positions and atomic displacement parameter tables are deposited as Supplementary Material.

Table I. Comparison between Bond Lengths (Å) and Bond Angles (deg) in I and II

	I	II
O(1)–C(6)	1.206 (3)	1.219 (3)
O(2)–C(7)	1.206 (3)	1.212 (3)
N(1)–N(3)	1.452 (2)	1.467 (3)
N(1)–C(1)	1.511 (3)	1.490 (4)
N(1)–C(6)	1.392 (3)	1.389 (3)
N(2)–C(6)	1.376 (3)	1.377 (3)
N(2)–C(7)	1.372 (3)	1.379 (4)
N(2)–C(8)	1.454 (3)	1.463 (3)
N(3)–C(4)	1.516 (3)	1.491 (4)
N(3)–C(7)	1.393 (3)	1.393 (3)
C(1)–C(2)	1.504 (3)	1.543 (3)
C(1)–C(5)	1.518 (4)	1.525 (5)
C(2)–C(3)	1.331 (4)	1.559 (5)
C(3)–C(4)	1.505 (3)	1.542 (3)
C(4)–C(5)	1.524 (3)	1.543 (3)
N(3)–N(1)–C(1)	104.3 (1)	104.8 (2)
N(3)–N(1)–C(6)	107.0 (1)	106.8 (2)
C(1)–N(1)–C(6)	120.3 (2)	120.2 (2)
C(6)–N(2)–C(7)	111.2 (2)	111.3 (2)
C(6)–N(2)–C(8)	124.2 (2)	123.9 (2)
C(7)–N(2)–C(8)	124.4 (2)	124.8 (2)
N(1)–N(3)–C(4)	104.9 (1)	104.6 (2)
N(1)–N(3)–C(7)	107.0 (1)	107.0 (2)
C(4)–N(3)–C(7)	119.7 (2)	120.7 (2)
N(1)–C(1)–C(2)	106.2 (2)	105.8 (2)
N(1)–C(1)–C(5)	98.7 (2)	101.9 (2)
C(2)–C(1)–C(5)	101.1 (2)	102.6 (2)
C(1)–C(2)–C(3)	107.0 (2)	102.8 (2)
C(2)–C(3)–C(4)	107.1 (2)	102.2 (2)
N(3)–C(4)–C(3)	105.9 (1)	105.9 (2)
N(3)–C(4)–C(5)	98.1 (2)	101.9 (2)
C(3)–C(4)–C(5)	100.8 (2)	102.4 (2)
C(1)–C(5)–C(4)	93.4 (2)	93.0 (2)
O(1)–C(6)–N(1)	126.4 (2)	126.4 (2)
O(1)–C(6)–N(2)	126.6 (2)	126.5 (2)
N(1)–C(6)–N(2)	106.9 (1)	107.1 (2)
O(2)–C(7)–N(2)	127.0 (2)	126.7 (2)
O(2)–C(7)–N(3)	126.0 (2)	126.5 (3)
N(2)–C(7)–N(3)	107.0 (2)	106.8 (2)

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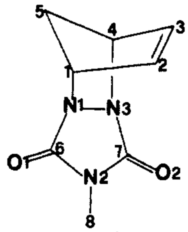
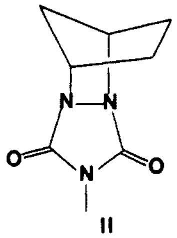
(1) Nelsen, S. F. *Acc. Chem. Res.* **1978**, *11*, 14.
(2) Shvo, Y. *The Chemistry of Hydrazo, Azo, and Azoxy Groups, Part 2*; patai, S., Ed.; Wiley: New York, pp 1017–1095.
(3) Offereins, B.; Altona, C.; Romers, C. *Acta Crystallogr.; Sect. B: Struct. Crystallog. Cryst. Chem.* **1973**, *B29*, 2098.



I



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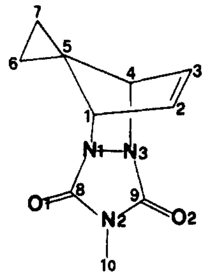
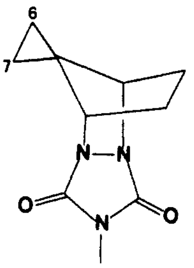
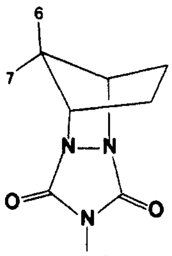


III



IV



V

The principal changes in geometry near the hydrazine nitrogens between the diazabicycloheptyl compounds reported here and the diazabicyclooctyl compounds previously reported[4] are seen in the comparison of the cyclopentadiene adduct I with the cyclohexadiene adduct VII shown in Figure 6 (the crystal structure is described later in this paper). The degree of flattening at N may be described in these systems either by the angle between the two planes joined at the NN bond, γ, or by the average of the bond angles at these nitrogen atoms, α_{av}. It is seen that decreasing the size of the saturated bridge from the two carbons of VII to the one of I significantly increases the pyramidality at nitrogen, α_{av} decreasing by 2.7° (corresponding to one quarter of the way from pure sp^3 lone pair hybridization) and the interplanar angle by 5.8°. The principal bond angle change at nitrogen is a 6.8° decrease in the C(1)NN angle, but the other two angles at the nitrogen atom also decrease slightly (0.6°) in response to the change in the bicyclic ring size which forces the C(1)NN angle to decrease sharply. Increased bending at nitrogen and hence an increase in the s character of the lone pair hybridization in I compared to VII is accompanied by an increase in the bond lengths to nitrogen, the C(1)N and NN bonds increasing by 0.020 and 0.019 Å, respectively. The conjugated N—C(═O) bond increases less than half as much, 0.008 Å, and the length of the remote N(2)C(═O) bonds does not change significantly. The observed bond lengths of I are successfully reproduced by the linear regression formula containing α_{av} which was derived from 27 diazabicyclooctane-containing adducts (eq 6 and Table III of ref 4); the only deviation larger than the uncertainty quoted is that of the $N_2C(=O)$ bond, calculated to be 0.008 Å longer than that observed for I, although it should also be noted that the calculated value is 0.003 Å too large for VII which is larger than the errors for any of the other calculated bond lengths. Interestingly, the bond angles about the hydrazine nitrogens calculated by using the same linear regression formula do not work well at all for I, giving a calculated C(1)NN angle 6.3° too large and a C(1)NC(═O) angle 7.4° too small. Perhaps not surprisingly, when the bond is forced to change as large an amount as is required by going from a bicyclooctyl to a bicycloheptyl framework, the regression formula no longer works. The angles inside the conjugated triazolidinedione ring change little and are successfully calculated by linear regression formula.

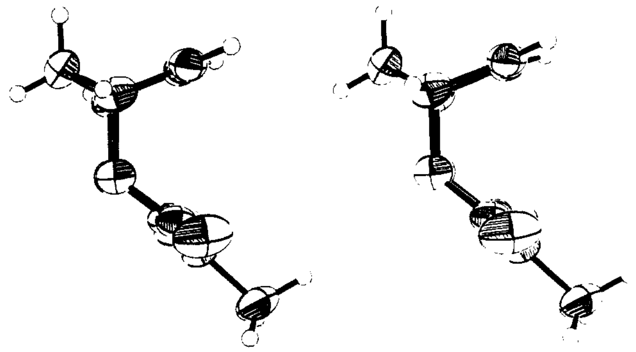


Figure 1. Stereoscopic view of I.

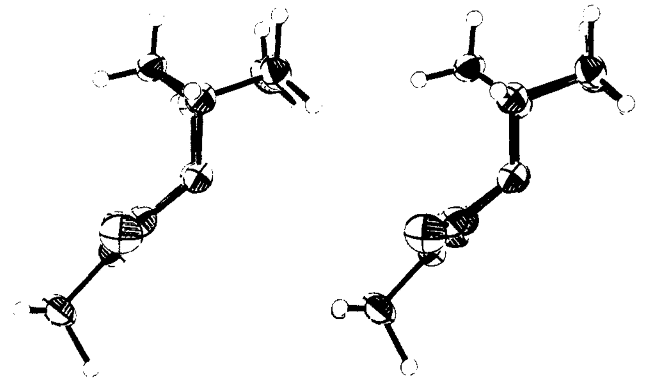


Figure 2. Stereoscopic view of II.

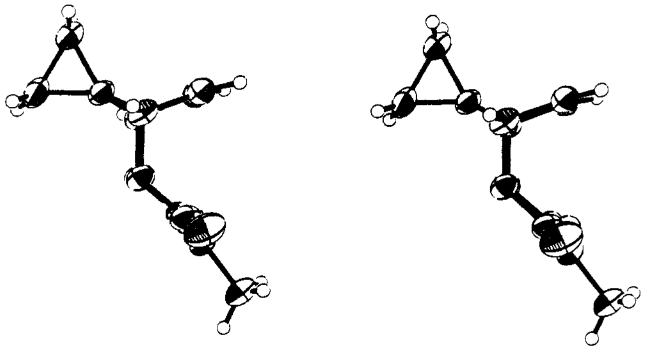


Figure 3. Stereoscopic view of III.

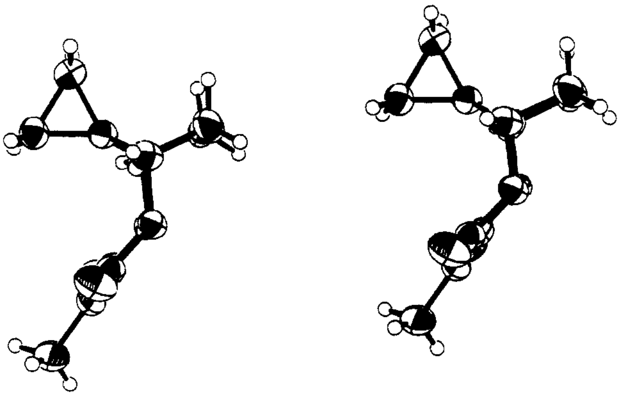


Figure 4. Stereoscopic view of one of the two independent molecules in IV.

The overall amounts of bend at nitrogen in I–V change relatively little with structure, the range in α_{av} being 110.5–112.0° and in

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(4) Kaftory, M.; Agmon, I. *J. Am. Chem. Soc.* **1984**, *106*, 7785.

(5) The atomic numbering throughout this paper is not corresponding to one of the accepted chemical conventions.

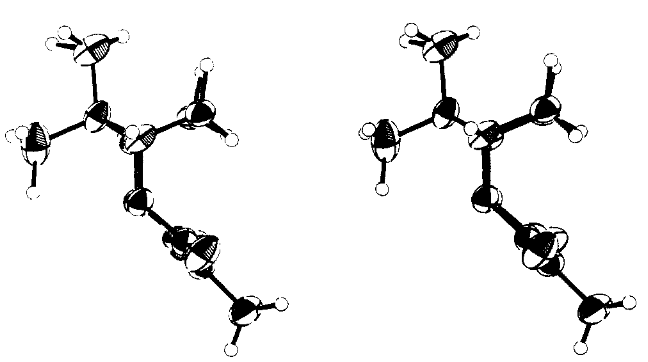
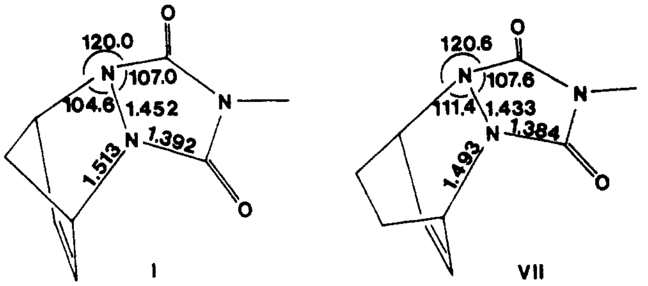


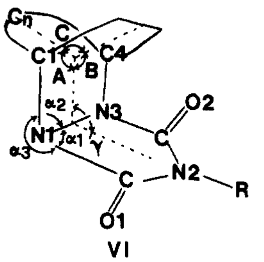
Figure 5. Stereoscopic view of V.



I		VII
110.5	α_{av} °	113.2
128.3	γ °	134.1

Figure 6. Comparison of the geometries about the hydrazine nitrogens for I and VII.

γ 128.3–135.5°. Perhaps the most interesting result observed is the sensitivity of the direction of the bend at the hydrazine unit to small changes in steric hindrance in the bicycloheptyl portion of the molecule. The unsaturated bicyclic compounds I and III have the triazolidine ring bent toward the unsaturation at C(2)=C(3) (endo bend), but their hydrogenated analogues are bent toward the one atom bridge, C(5) (exo bend). Hydrogenation of the spirocyclopropyl ring of IV to give the C(5) dimethyl compound V reverses the direction of bend again; V is endo bent. In all cases, the direction of bend observed in the crystal corresponds to the least hindered conformation. The change in geometry of the bicyclic rings may be most easily seen by considering the angles between the planes joining at the C(1), C(4), axis (see VI). Hydrogenation of I to II and III to IV increases angle *A* by 6.2 and 6.8°, respectively, while it decreases angle *C* by 4.3 and 4.9°. The intramolecular distances of C(5) and the midpoint of the C(2)–C(3) bond to the CO groups range between 3.06 and 3.14 Å in compounds I–IV. This similarity indicates that the carbon atoms [C(2),C(3),C(5)] of the bicycloheptyl system (from both sides of the triazolidinedione ring) have similar steric effects and therefore probably have no effect on the configuration. The influence of the hydrogen hindrance may be expressed by the relative distances of the lowest atoms (at the cyclopentane(ene) ring) from a plane passing through N(1),N(3) and perpendicular to the bonds C(1)–N(1),C(4)–N(3) (see Table III). In both compounds I and III the hydrogen atoms at C(5) (in I) and at C(6) (in III) are closer to the plane described above by ~0.5 Å than the hydrogens at the unsaturated bond [atoms C(2),C(3)]; therefore, the bend is toward C(2)=C(3). The reverse situation occurs in compounds II and IV, where the bent is opposite to that of C(2)–C(3) (being saturated). In compound V, on the other hand, the triazolidinedione is bent toward the saturated bonds because of the steric repulsion imposed by a hydrogen atom bonded to a methyl group (H72).



VI

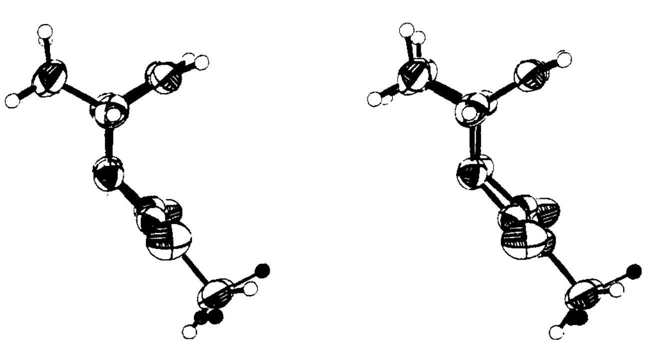


Figure 7. Stereoscopic view of VII.

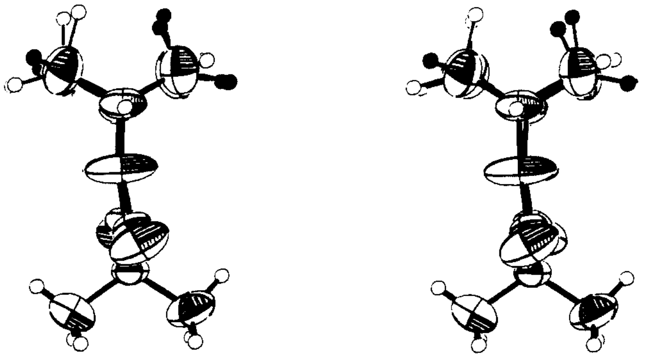


Figure 8. Stereoscopic view VIII.

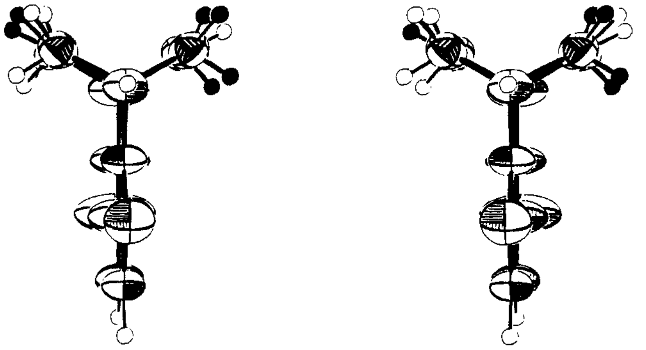


Figure 9. Stereoscopic view of IX.

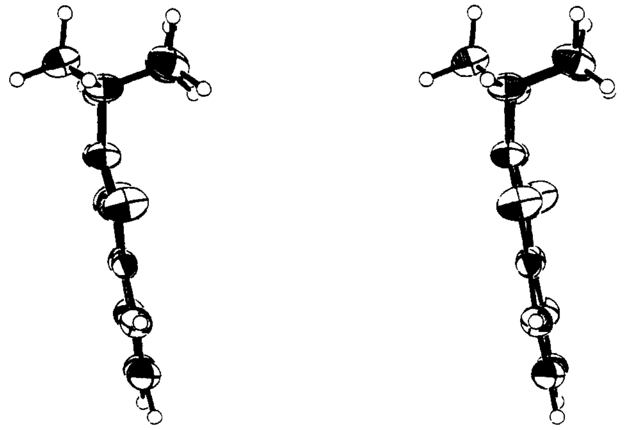


Figure 10. Stereoscopic view of X.

B. Conjugative-Electronic Effect on the Configuration. Molecular Structures. The average bond lengths and angles and the differences between the two chemically equivalent quantities (follow the slash) are given in VII–XIII (for atomic numbering

Table II. Comparison between Bond Lengths (Å) and Bond Angles (deg) in III–V

	III	IV(A)	IV(B)	V
O(1)–C(8)	1.202 (2)	1.204 (3)	1.207 (3)	1.184 (4)
O(2)–C(9)	1.207 (2)	1.208 (3)	1.215 (3)	1.211 (5)
N(1)–N(3)	1.442 (2)	1.460 (3)	1.453 (2)	1.450 (4)
N(1)–C(1)	1.524 (2)	1.496 (3)	1.494 (3)	1.481 (4)
N(1)–C(8)	1.393 (2)	1.377 (3)	1.388 (3)	1.382 (4)
N(2)–C(8)	1.382 (2)	1.393 (3)	1.387 (3)	1.389 (4)
N(2)–C(9)	1.387 (2)	1.387 (3)	1.383 (3)	1.402 (5)
N(2)–C(10)	1.459 (3)	1.458 (3)	1.453 (4)	1.453 (5)
N(3)–C(4)	1.518 (2)	1.508 (3)	1.491 (3)	1.492 (4)
N(3)–C(9)	1.388 (2)	1.377 (3)	1.381 (3)	1.379 (4)
C(1)–C(2)	1.510 (2)	1.530 (4)	1.529 (4)	1.544 (5)
C(1)–C(5)	1.530 (2)	1.506 (4)	1.515 (3)	1.540 (5)
C(2)–C(3)	1.334 (3)	1.570 (5)	1.552 (5)	1.545 (5)
C(3)–C(4)	1.511 (3)	1.518 (4)	1.531 (4)	1.505 (6)
C(4)–C(5)	1.516 (2)	1.507 (3)	1.516 (3)	1.558 (5)
C(5)–C(6)	1.487 (3)	1.502 (4)	1.488 (3)	1.522 (6)
C(5)–C(7)	1.488 (3)	1.496 (4)	1.478 (3)	1.537 (7)
C(6)–C(7)	1.522 (3)	1.526 (4)	1.511 (4)	
N(3)–N(1)–C(1)	105.1 (1)	104.8 (1)	105.1 (1)	105.2 (2)
N(3)–N(1)–C(8)	107.7 (1)	107.4 (1)	107.4 (1)	108.4 (2)
C(1)–N(1)–C(8)	121.6 (1)	120.6 (2)	122.4 (2)	123.2 (3)
C(8)–N(2)–C(9)	111.2 (1)	110.9 (2)	111.1 (2)	111.8 (3)
C(8)–N(2)–C(10)	124.7 (2)	124.7 (2)	123.6 (2)	123.6 (3)
C(9)–N(2)–C(10)	124.1 (2)	123.9 (2)	125.0 (2)	124.0 (3)
N(1)–N(3)–C(4)	105.1 (1)	104.6 (1)	105.2 (2)	105.0 (2)
N(1)–N(3)–C(9)	107.6 (1)	107.6 (2)	107.5 (2)	108.0 (2)
C(4)–N(3)–C(9)	120.3 (1)	121.7 (2)	122.7 (2)	122.2 (3)
N(1)–C(1)–C(2)	105.6 (1)	105.9 (2)	105.7 (2)	107.7 (2)
N(1)–C(1)–C(5)	96.6 (1)	100.6 (1)	100.7 (1)	99.4 (3)
C(2)–C(1)–C(5)	100.9 (1)	102.6 (2)	102.0 (2)	103.6 (2)
C(1)–C(2)–C(3)	107.6 (1)	102.5 (2)	102.8 (2)	102.4 (3)
C(2)–C(3)–C(4)	107.2 (1)	102.2 (2)	102.9 (2)	103.4 (3)
N(3)–C(4)–C(3)	105.6 (1)	105.8 (2)	105.2 (2)	107.9 (2)
N(3)–C(4)–C(5)	97.1 (1)	100.6 (2)	100.8 (2)	98.9 (2)
N(3)–C(4)–C(5)	101.5 (1)	103.0 (2)	102.0 (2)	104.1 (3)
C(1)–C(5)–C(4)	94.5 (1)	95.0 (2)	94.9 (2)	91.9 (2)
C(1)–C(5)–C(6)	126.5 (1)	125.8 (2)	125.3 (2)	113.8 (3)
C(1)–C(5)–C(7)	125.0 (1)	125.7 (2)	125.6 (2)	113.7 (3)
C(4)–C(5)–C(6)	125.6 (1)	125.0 (2)	124.7 (2)	113.0 (3)
C(4)–C(5)–C(7)	125.7 (1)	125.7 (2)	126.8 (2)	113.3 (3)
C(6)–C(5)–C(7)	61.5 (1)	61.2 (2)	61.3 (1)	110.2 (4)
C(5)–C(6)–C(7)	59.2 (1)	59.2 (2)	59.1 (1)	
C(5)–C(7)–C(6)	59.2 (1)	59.6 (2)	59.7 (1)	
O(1)–C(8)–N(1)	127.4 (2)	127.7 (2)	126.7 (2)	127.1 (3)
O(1)–C(8)–N(2)	126.4 (2)	125.9 (2)	127.2 (2)	127.4 (3)
N(1)–C(8)–N(2)	106.2 (1)	106.3 (2)	106.0 (2)	105.4 (2)
O(2)–C(9)–N(2)	127.1 (1)	126.7 (2)	126.3 (2)	126.0 (3)
O(2)–C(9)–N(3)	126.7 (1)	126.8 (2)	127.2 (2)	128.6 (3)
N(2)–C(9)–N(3)	106.2 (1)	106.4 (1)	106.4 (2)	105.3 (3)

Table III. Comparison of Relevant Geometrical Parameters

compd	α_{av} (deg)	γ (deg)	C–CO distances (Å)		H to P[a] distances (Å)		bent toward
I	110.5	128.3	C(2)–C(6)O	2.891	H(2)	2.30	
			C(3)–C(7)O	2.883	H(3)	2.18	
					H(51)	1.57	C(2)=C(3)
II	110.7	128.9	C(5)–C(6)O	3.094	H(21)	1.34	
			C(5)–C(7)O	3.142	H(31)	1.39	
					H(51)	1.83	C(5)
III	111.2	132.9	C(2)–C(8)O	2.942	H(2)	2.21	
			C(3)–C(9)O	2.900	H(3)	2.18	
					H(62)	1.54	C(2)=C(3)
IV(A)	111.7	135.3	C(5)–C(8)O	3.135	H(22)	1.54	
			C(5)–C(9)O	3.144	H(32)	1.38	
					H(72)	1.96	C(5)
IV(B)	111.1	133.2	C(5)–C(8)O	3.076	H(21)	1.48	
			C(5)–C(9)O	3.124	H(32)	1.39	
					H(72)	1.86	C(5)
V	112.0	135.5	C(2)–C(8)O	2.978	H(22)	1.37	
			C(3)–C(9)O	2.925	H(31)	1.56	
					H(71)	0.25	C(2)–C(3)

[a] P is the plane defined in the text.

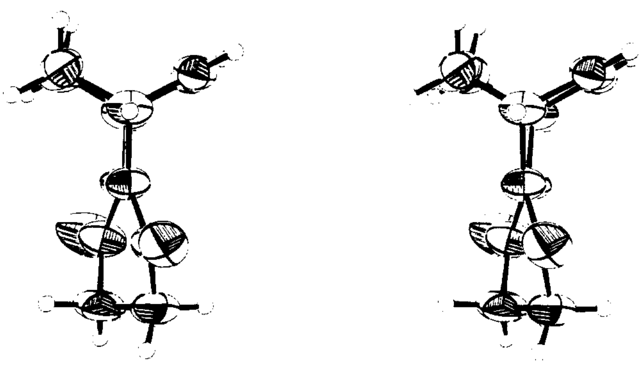


Figure 11. Stereoscopic view of XI.

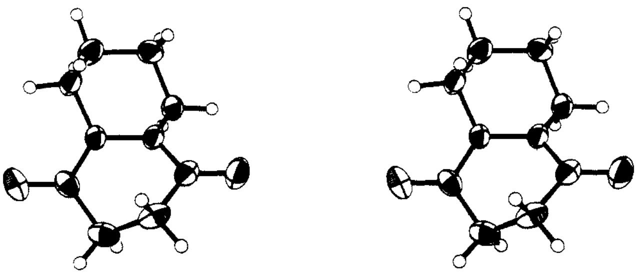


Figure 12. Stereoscopic view of XII.

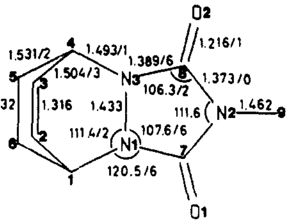
Table IV. Bond Lengths (Å) and Angles (deg) for Compound VII

O(1)–C(7)	1.215 (2)	N(3)–C(4)	1.493 (2)
O(2)–C(8)	1.216 (2)	N(3)–C(8)	1.382 (2)
N(1)–N(3)	1.433 (2)	C(1)–C(2)	1.502 (3)
N(1)–C(1)	1.492 (2)	C(1)–C(6)	1.530 (3)
N(1)–C(7)	1.386 (2)	C(2)–C(3)	1.316 (3)
N(2)–C(7)	1.373 (2)	C(3)–C(4)	1.505 (3)
N(2)–C(8)	1.373 (2)	C(4)–C(5)	1.532 (3)
N(2)–C(9)	1.462 (3)	C(5)–C(6)	1.532 (4)
N(3)–N(1)–C(1)	111.5 (1)	C(2)–C(3)–C(4)	113.6 (1)
N(3)–N(1)–C(7)	107.3 (1)	N(3)–C(4)–C(3)	107.1 (1)
C(1)–N(1)–C(7)	120.2 (1)	N(3)–C(4)–C(5)	105.7 (1)
C(7)–N(2)–C(8)	111.6 (1)	C(3)–C(4)–C(5)	109.7 (2)
C(7)–N(2)–C(9)	123.6 (2)	C(4)–C(5)–C(6)	109.1 (2)
C(8)–N(2)–C(9)	124.7 (2)	C(1)–C(6)–C(5)	108.7 (2)
N(1)–N(3)–C(4)	111.3 (1)	O(1)–C(7)–N(1)	126.6 (2)
N(1)–N(3)–C(8)	107.9 (1)	O(1)–C(7)–N(2)	126.9 (2)
C(4)–N(3)–C(8)	120.8 (1)	N(1)–C(7)–N(2)	106.4 (1)
N(1)–C(1)–C(2)	107.8 (1)	O(2)–C(8)–N(2)	127.2 (2)
N(1)–C(1)–C(6)	105.9 (1)	O(2)–C(8)–N(3)	126.6 (2)
C(2)–C(1)–C(6)	109.0 (2)	N(2)–C(8)–N(3)	106.2 (1)
C(1)–C(2)–C(3)	113.8 (2)		

Table V. Bond Lengths (Å) and Angles (deg) for Compound VIII

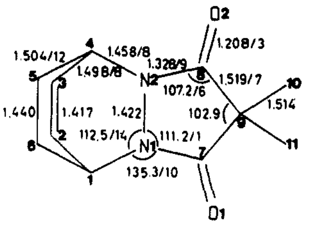
O(1)–C(7)	1.206 (4)	C(1)–C(6)	1.510 (6)
O(2)–C(9)	1.209 (4)	C(2)–C(3)	1.417 (7)
N(1)–N(2)	1.422 (5)	C(3)–C(4)	1.494 (6)
N(1)–C(1)	1.454 (4)	C(4)–C(5)	1.498 (6)
N(1)–C(7)	1.323 (4)	C(5)–C(6)	1.440 (7)
N(2)–C(4)	1.462 (4)	C(7)–C(8)	1.522 (4)
N(2)–C(9)	1.314 (4)	C(8)–C(9)	1.515 (4)
C(1)–C(2)	1.502 (6)	C(8)–C(10)	1.514 (7)
N(2)–N(1)–C(1)	113.2 (2)	C(3)–C(4)–C(5)	107.5 (3)
N(2)–N(1)–C(7)	111.1 (3)	C(4)–C(5)–C(6)	111.5 (4)
C(1)–N(1)–C(7)	134.8 (3)	C(1)–C(6)–C(5)	111.2 (3)
N(1)–N(2)–C(4)	111.8 (2)	O(1)–C(7)–N(1)	124.7 (3)
N(1)–N(2)–C(9)	111.2 (2)	O(1)–C(7)–C(8)	128.3 (3)
C(4)–N(2)–C(9)	135.8 (3)	N(1)–C(7)–C(8)	106.9 (2)
N(1)–C(1)–C(2)	107.4 (3)	C(7)–C(8)–C(9)	102.9 (2)
N(1)–C(1)–C(6)	105.8 (3)	C(7)–C(8)–C(10)	110.0 (3)
C(2)–C(1)–C(6)	107.1 (3)	C(9)–C(8)–C(10)	109.9 (3)
C(1)–C(2)–C(3)	111.7 (4)	O(2)–C(9)–N(2)	124.4 (3)
C(2)–C(3)–C(4)	112.2 (4)	O(2)–C(9)–C(8)	128.1 (3)
N(2)–C(4)–C(3)	107.7 (3)	N(2)–C(9)–C(8)	107.5 (2)
N(2)–C(4)–C(5)	106.0 (3)		

see note 5 in the references list). Stereoscopic drawings of the seven compounds reported here (VII–XIII) are shown in Figures 7–13, respectively; bond lengths and angles are given in Tables IV–X, and atomic positions and atomic displacement parameters have been deposited as supplementary material.



α_{av} 113.2°
Y 134.1°

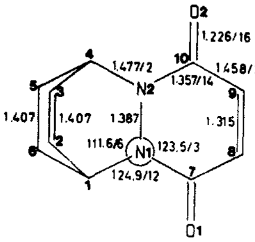
VII



α_{av} 119.7°
Y 169.9°

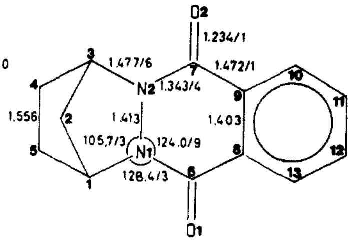
VIII

In compounds VIII and IX a similar type of disorder was detected, which may be described as a superposition of two molecules related by a mirror plane passing through C(1), C(4), N(1), N(2), a failure to distinguish between the saturated and unsaturated two carbon bridges when the crystals assemble. However, while the disorder imposed crystallographic mirror symmetry in IX, causing an averaging of the pure double bond and single bonds [between C(2)–C(3) and C(5)–C(6)] to 1.407 Å, there is not such a mirror plane in VIII. The bond lengths observed were 1.417 and 1.439 Å, still intermediate between single and double bond values, indicating that similar disorder exists but that the units are not as completely random in the crystal. The methyl group hydrogens in VII were found to adopt two different conformations in equal probability.



α_{av} 120.0°
Y 180.0°

IX

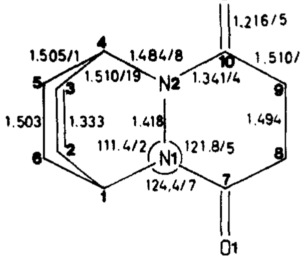


α_{av} 119.2°
Y 164.8°

X

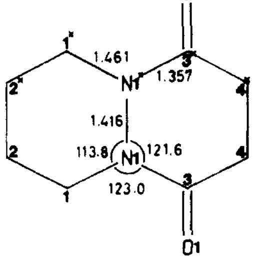
Both IX and XI have a monocyclic four carbon bridge between the nitrogens, but the C(8)–C(9) double bond of IX resists twisting, and IX has planar monocyclic ring (the disordered molecule has a crystallographic mirror symmetry plane). The corresponding ring in XI, which has a C(8)–C(9) single bond, adopts a twist-boat conformation, allowing the hydrazine lone pairs to twist out of coplanarity.

XII has a crystallographic twofold axis.



α_{av} 119.2°
C1-N1-N2-C4 3.0°
C7-N1-N2-C10 37.3°

XI



α_{av} 119.5°
C1-N1-N1*-C1* 55.9°
C3-N1-N1*-C1* 27.7°

XII

Discussion

A set of 27 2,3-diazabicyclo[2.2.2]octanes in which the nitrogens were incorporated in a triazolidinedione ring (VI, $n = 2$) has been thoroughly studied structurally[4] and is used as a reference system for the compounds described here. Examination of the reference system data shows two main facts: (1) The set of molecules lacked examples in which the N–N′ hydrazine nitrogen atoms were coplanar with their bonded C atoms. Despite the large number of structures, the largest α_{av} [$\alpha_{av} = \Sigma$ valence bond angles at N(1) {or N(3)}/3] observed was 117.9°, compared with 120° for planar N atoms. (2) The few examples with relatively large α_{av} values were the more sterically hindered examples.

There is a clear trend toward flattening at nitrogen as the third bridge in triazolidinedione derivatives of 2,3-diazabicyclo[2.2.*n*] compounds is enlarged. The $n = 1$ compound XIV has α_{av} =

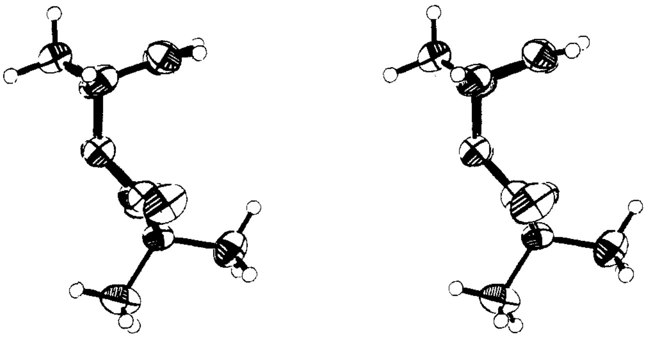


Figure 13. Stereoscopic view of XIII.

Table VI. Bond Lengths (Å) and Angles (deg) for Compound IX

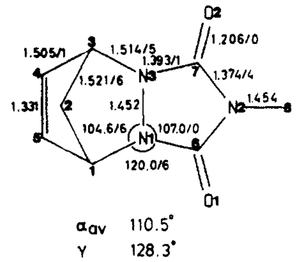
O(1)–C(7)	1.218 (5)	C(1)–C(2)	1.232 (4)
O(2)–C(10)	1.234 (7)	C(2)–C(3)	1.407 (6)
N(1)–N(2)	1.387 (4)	C(3)–C(4)	1.227 (5)
N(1)–C(1)	1.475 (5)	C(7)–C(8)	1.468 (7)
N(1)–C(7)	1.364 (5)	C(8)–C(9)	1.315 (8)
N(2)–C(4)	1.479 (5)	C(9)–C(10)	1.448 (8)
N(2)–C(10)	1.350 (6)		

N(2)–N(1)–C(1)	111.9 (3)	C(2)–C(3)–C(4)	113.6 (4)
N(2)–N(1)–C(7)	123.8 (3)	N(2)–C(4)–C(3)	112.4 (3)
C(1)–N(1)–C(7)	124.3 (3)	O(1)–C(7)–N(1)	121.9 (4)
N(1)–N(2)–C(4)	111.3 (3)	O(1)–C(7)–C(8)	124.7 (4)
N(1)–N(2)–C(10)	123.2 (4)	N(1)–C(7)–C(8)	113.4 (3)
C(4)–N(2)–C(10)	125.5 (4)	C(7)–C(8)–C(9)	122.2 (4)
N(1)–C(1)–C(2)	110.2 (3)	C(8)–(9)–C(10)	123.0 (5)
C(1)–C(2)–C(3)	117.8 (4)	O(2)–C(10)–N(2)	121.4 (5)
		O(2)–C(10)–C(9)	124.1 (5)
		N(2)–C(10)–C(9)	114.5 (4)

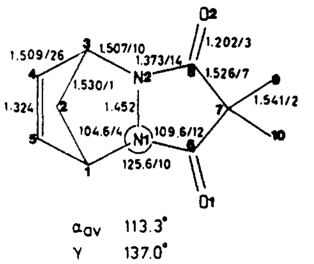
Table VII. Bond Lengths (Å) and Angles (deg) for Compound X

O(1)–C(6)	1.234 (3)	C(3)–C(4)	1.529 (4)
O(2)–C(7)	1.233 (3)	C(4)–C(5)	1.513 (4)
N(1)–N(2)	1.413 (2)	C(6)–C(8)	1.471 (3)
N(1)–C(1)	1.480 (3)	C(7)–C(9)	1.472 (3)
N(1)–C(6)	1.341 (3)	C(8)–C(9)	1.403 (3)
N(2)–C(4)	1.474 (3)	C(8)–C(13)	1.393 (3)
N(2)–C(7)	1.345 (3)	C(9)–C(10)	1.395 (3)
C(1)–C(2)	1.529 (4)	C(10)–C(11)	1.375 (4)
C(1)–C(5)	1.518 (3)	C(11)–C(12)	1.376 (4)
C(2)–C(3)	1.556 (4)	C(12)–C(13)	1.380 (3)

N(2)–N(1)–C(1)	105.8 (1)	O(1)–C(6)–C(8)	123.8 (2)
N(2)–N(1)–C(6)	124.4 (2)	N(1)–C(6)–C(8)	114.7 (2)
C(1)–N(1)–C(6)	128.2 (2)	O(2)–C(7)–N(2)	120.9 (2)
N(1)–N(2)–C(4)	105.5 (1)	O(2)–C(7)–C(9)	124.3 (2)
N(1)–N(2)–C(7)	123.5 (2)	N(2)–C(7)–C(9)	114.8 (2)
C(4)–N(2)–C(7)	128.5 (2)	C(6)–C(8)–C(9)	120.8 (2)
N(1)–C(1)–C(2)	106.4 (2)	C(6)–C(8)–C(13)	119.9 (2)
N(1)–C(1)–C(5)	99.8 (2)	C(9)–C(8)–C(13)	119.3 (2)
C(2)–C(1)–C(5)	102.7 (2)	C(7)–C(9)–C(8)	121.0 (2)
C(1)–C(2)–C(3)	102.5 (2)	C(7)–C(9)–C(10)	119.2 (2)
C(2)–C(3)–C(4)	102.2 (2)	C(8)–C(9)–C(10)	119.8 (2)
N(2)–C(4)–C(3)	107.1 (2)	C(9)–C(10)–C(11)	119.8 (2)
N(2)–C(4)–C(5)	100.0 (2)	C(10)–C(11)–C(12)	120.8 (2)
C(3)–C(4)–C(5)	103.1 (2)	C(11)–C(12)–C(13)	120.3 (2)
C(1)–C(5)–C(4)	93.5 (2)	C(8)–C(13)–C(12)	120.1 (2)
O(1)–C(6)–N(1)	121.5 (2)		

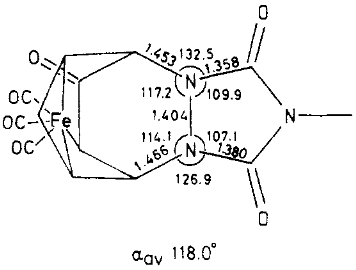


XIV



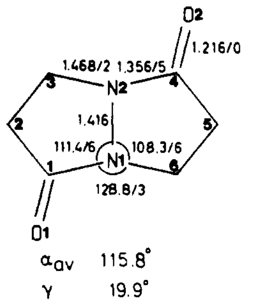
XIII

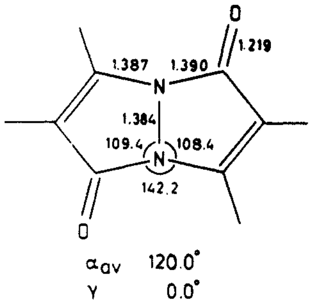
110.5°, the n = 2 compound VII has α_{av} = 113.2°, and the iron-containing n = 3 compound XV has α_{av} = 118.0°.[6] There is relatively little variation in the NNC angle in the triazolidinedione ring (α_1 of structure VI), which is structurally constant for this series and varies from 107.0 to 109.9°, but the NNC angle in the bicyclic portion of the molecule varies more substantially as the size of the third bridge of the bicyclic system is increased from 104.6° in XIV (n = 1) to 111.4° in VII (n = 2) and an average of 115.7° in XV (n = 3). The external CNC angle varies in the same order in this series, 120.0, 120.5 and 129.7°, respectively, although the n = 1 and 2 examples have quite similar CNC angles. We believe that this comparison makes it clear that restriction of one NNC angle, as expected, causes greater pyramidality at nitrogen.



XV

Structural studies[7] on the "bimanes" prepared by Kowsower's group have demonstrated that even when both NNC angles are restricted to angles under 110° by being in five-membered rings as in XVI and its analogues, the nitrogens are planar when each is conjugated to two carbonyl substituents. A way to flatten the nitrogens of these N,N′-diacyl tricyclic hydrazines, which does not involve change in ring size or conjugation with carbonyl groups at both substituents on each nitrogen, involves replacement of the urea-type nitrogen of the triazolidinedione ring (N(2) in VI) by a carbon atom. Removal of N(2) from conjugation with the carbonyl groups makes the carbonyl conjugation with the hydrazine nitrogens more important, leading to significant flattening. In the n = 1 series, α_{av} increases from 110.5° in triazolidinedione XIV to 113.3° in pyrazolidinedione XIII [that is, upon replacing NCH_3 by $C(CH_3)_2$]. This corresponds to change in the formal hybridization[8] of the nitrogen lone pair from $sp^{3.5}$ to $sp^{5.7}$ and the fractional s character f_s from 0.22 to 0.15. The corresponding change in pyramidality at nitrogen in the n = 2 series where the triazolidinedione example VII has α_{av} = 113.2° may be even greater, but the disorder observed for the pyrazolidinedione example VIII ensures that the observed α_{av} value of 119.7° is larger than that actually present in a single molecule, and we are unable to accurately estimate α_{av} for VIII from our data.





XVI

Table VIII. Bond Lengths (Å) and Angles (deg) for Compound XI

O(1)–C(7)	1.213 (6)	C(1)–C(6)	1.505 (7)
O(2)–C(10)	1.218 (7)	C(2)–C(3)	1.333 (7)
N(1)–N(2)	1.418 (5)	C(3)–C(4)	1.519 (7)
N(1)–C(1)	1.488 (5)	C(4)–C(5)	1.504 (8)
N(1)–C(7)	1.343 (5)	C(5)–C(6)	1.503 (8)
N(2)–C(4)	1.480 (5)	C(7)–C(8)	1.507 (8)
N(2)–C(10)	1.339 (6)	C(8)–C(9)	1.494 (9)
C(1)–C(2)	1.500 (7)	C(9)–C(10)	1.513 (8)
N(2)–N(1)–C(1)	111.3 (3)	N(2)–C(4)–C(5)	107.9 (4)
N(2)–N(1)–C(7)	122.0 (3)	C(3)–C(4)–C(5)	108.2 (4)
C(1)–N(1)–C(7)	124.0 (3)	C(4)–C(5)–C(6)	108.9 (4)
N(1)–N(2)–C(4)	111.5 (3)	C(1)–C(6)–C(5)	109.9 (4)
N(1)–N(2)–C(10)	121.5 (3)	O(1)–C(7)–N(1)	122.8 (4)
C(4)–N(2)–C(10)	124.7 (3)	O(1)–C(7)–C(8)	124.5 (4)
N(1)–C(1)–C(2)	106.2 (3)	N(1)–C(7)–C(8)	112.7 (4)
N(1)–C(1)–C(6)	107.3 (4)	C(7)–C(8)–C(9)	111.4 (4)
C(2)–C(1)–C(6)	109.1 (3)	C(8)–C(9)–C(10)	112.0 (5)
C(1)–C(2)–C(3)	113.2 (4)	O(2)–C(10)–N(2)	122.0 (5)
C(2)–C(3)–C(4)	112.4 (4)	O(2)–C(10)–C(9)	125.0 (5)
N(2)–C(4)–C(3)	107.1 (3)	N(2)–C(10)–C(9)	112.9 (4)

Table IX. Bond Lengths (Å) and Angles (deg) for Compound XII

O(1)–C(3)	1.216 (3)	C(1)–C(2)	1.520 (2)
N(1)–C(1)	1.462 (2)	C(2)–C(2*)	1.505 (4)
N(1)–C(3)	1.357 (3)	C(3)–C(4)	1.510 (3)
N(1)–N(1*)	1.416 (2)	C(4)–C(4*)	1.528 (5)
C(1)–N(1)–C(3)	123.0 (2)	O(1)–C(3)–N(1)	121.7 (2)
C(1)–N(1)–N(1*)	113.8 (1)	O(1)–C(3)–C(4)	124.3 (2)
C(3)–N(1)–N(1*)	121.6 (2)	N(1)–C(3)–C(4)	114.0 (2)
N(1)–C(1)–C(2)	110.5 (3)	C(3)–C(4)–C(4*)	108.2 (2)
C(1)–C(2)–C(2*)	110.7 (1)		

Table X. Bond Lengths (Å) and Angles (deg) for Compounx XIII

O(1)–C(6)	1.200 (4)	C(1)–C(5)	1.530 (5)
O(2)–C(8)	1.203 (4)	C(2)–C(3)	1.324 (6)
N(1)–N(2)	1.452 (3)	C(3)–C(4)	1.522 (5)
N(1)–C(1)	1.512 (3)	C(4)–C(5)	1.529 (4)
N(1)–C(6)	1.366 (4)	C(6)–C(7)	1.529 (3)
N(2)–C(4)	1.502 (3)	C(7)–C(8)	1.522 (4)
N(2)–C(8)	1.380 (3)	C(7)–C(9)	1.542 (4)
C(1)–C(2)	1.496 (4)	C(7)–C(10)	1.540 (4)
N(2)–N(1)–C(1)	104.4 (2)	C(1)–C(5)–C(4)	92.7 (2)
N(2)–N(1)–C(6)	110.2 (2)	O(1)–C(6)–N(1)	125.8 (3)
C(1)–N(1)–C(6)	125.1 (2)	O(1)–C(6)–C(7)	126.8 (2)
N(1)–N(2)–C(4)	104.8 (2)	N(1)–C(6)–C(7)	107.4 (2)
N(1)–N(2)–C(8)	109.0 (2)	C(6)–C(7)–C(8)	102.1 (2)
C(4)–N(2)–C(8)	126.1 (2)	C(6)–C(7)–C(9)	110.9 (2)
N(1)–C(1)–C(2)	104.6 (3)	C(6)–C(7)–C(10)	110.2 (3)
N(1)–C(1)–C(5)	98.7 (2)	C(8)–C(7)–C(9)	110.4 (2)
C(2)–C(1)–C(5)	101.6 (2)	C(8)–C(7)–C(10)	111.0 (2)
C(1)–C(2)–C(3)	108.3 (3)	C(9)–C(7)–C(10)	111.8 (3)
C(2)–C(3)–C(4)	106.0 (3)	O(2)–C(8)–N(2)	124.3 (2)
N(2)–C(4)–C(3)	105.4 (2)	O(2)–C(8)–C(7)	127.8 (3)
N(2)–C(4)–C(5)	98.6 (2)	N(2)–C(8)–C(7)	107.9 (2)
C(3)–C(4)–C(5)	101.5 (3)		

Compounds IX, XI, XIII, and XII combine the effects of less restricted NNC angles in both N,N′ rings and the presence of a carbonyl group conjugated only with a hydrazine nitrogen atom, and all are probably very flat at nitrogen. The random disorder

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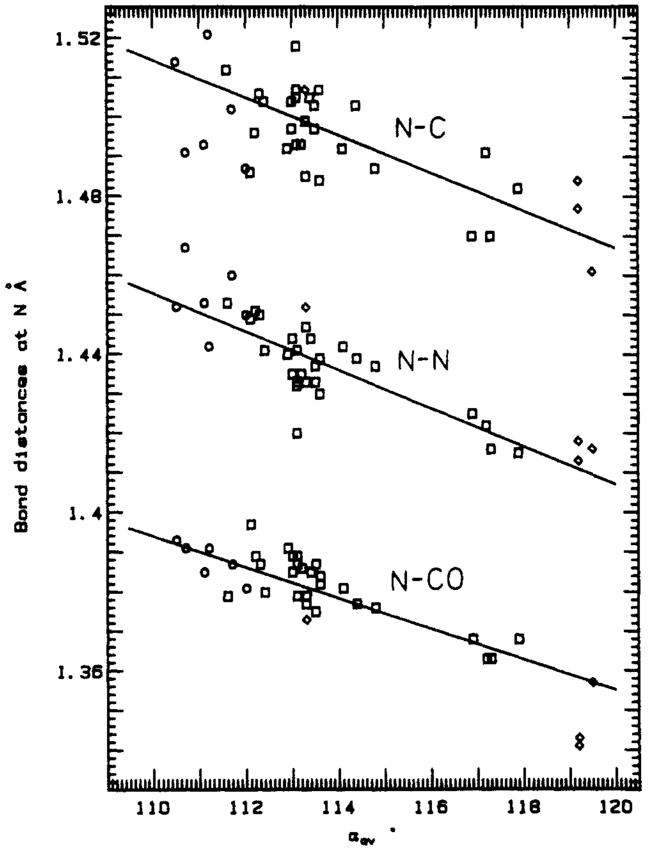

Figure 14. Variation of the bond lengths (Å) involving hydrazine's nitrogen atoms, with the average bond angle around them (α_{av}°).

in IX precludes accurate measure of its true α_{av} value, but XI does not appear to be disordered like VIII and IX are (note that the C(2)–C(3) and C(5)–C(6) bond distances are close to C=C and C—C values, respectively), and XIII and XII do not have the problem of having the bridges which only differ in the number of hydrogen atoms at each carbon, which leads to such disorder. All three show α_{av} values in the 119.2–119.5° range, corresponding to formal nitrogen lone pair hybridization of sp^{60} to sp^{97} and f_s of 0.02–0.01. The degree of nonplanarity of the pyridazinedione rings varies substantially for these compounds. This ring of XI is in a twist-boat conformation with dihedral angle C(7)N(1), N(2)C(10) of 37.3°, but the benzo-substituted ring of XIII is nearly planar (dihedral angle C(6)N(1), N(2)C(7) = –1.8°), and the saturated pyridazinedione ring of XII, which is free to twist both CN,NC dihedral angles, has a twist angle C(1)N(1), N-(1)C(1) of 55.9° and a C(3)N(1), N(1)C(3) twist angle of 27.7°.

A plot of the bond lengths at the hydrazine nitrogens vs. α_{av} is shown in Figure 14. The lines are the extrapolated average values for the 2,3-diazabicyclo[2.2.2]octyltriazolidinediones VI, $n = 2$,[4] which are shown as the squares on the plot. Both the more bent VI, $n = 1$ compounds (see part A of this paper) shown as circles, and the flatter compounds which lack the nitrogen bridging the carbonyl groups which are discussed in part B in this paper, shown as diamonds, are seen to fall in the same sort of distribution range. α_{av} appears to provide a reasonable description of the hybridization at nitrogen, even when the ring sizes are changed. The individual bond angles at nitrogen do not correlate successfully with the bond lengths, because the internal angles α_1 and α_2 are determined principally by ring size and only secondarily by how pyramidal the nitrogen atoms are.

Conclusion

N,N'-Dialkyl-*N,N'*-diacyclohydrazines which have structures holding the hydrazine nitrogen lone pairs nearly coplanar have been shown to undergo great changes in the amount of pyramidality at the hydrazine nitrogens when rather modest structural changes are made. For example, the 2,3-diazabicyclo[2.2.1]heptyl bridged compound X, which has a six atom diketo ring, is essentially planar at nitrogen ($\alpha_{av} = 119.2°$, $f_s = 0.02$), but its five atom diketo ring analogue XIV is strongly bent ($\alpha_{av} = 110.5°$, $f_s = 0.22$). A combination of conjugational-electronic and steric effects as detailed above gives essentially a continuum of amounts of bend between these values, and as emphasized in Figure 14, the use of α_{av} to describe the amount of bend successfully correlates all three bond lengths at nitrogen over these hybridization changes.

Experimental Section

Compound Preparation. Methods for the preparation of compounds I, II, VII,[13a] VIII–XI, and XIII–XIV[13d] have been previously published.

III: compound III was prepared in 89% yield by room temperature addition of 1,3-cyclopentadiene-5-spirocyclopropane[13b] in CH_2Cl_2 to a CH_2Cl_2 solution of 4-methyl-1,2,4-triazoline-3,5-dione until the pink color just disappeared (mp 106–110 °C dec).

IV: compound IV[13c] was prepared in quantitative yield from III by atmospheric catalytic hydrogenation using a 5% Pd on $BaCO_3$ catalyst in ethyl acetate (mp 108–110 °C).

V: compound V was prepared in quantitative yield from III by atmospheric catalytic hydrogenation and hydrogenolysis using a Pt catalyst in 1:1 ethyl acetate/hexane (mp 114 °C).

Crystal Structure Data. Intensity data were measured with Philips PW 1100 four circle computer-controlled diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The crystal structures were solved either by Multan 80[9] or by Shelx 76[10] and refined by Shelx 76[10] with anisotropic vibrational parameters for O, N, and C atoms and isotropic for H atoms. The scattering factors for O, N, and C were taken from Cromer and Mann[11] and for H from Stewart et al.[12]

I: $C_8H_9N_3O_2$; monoclinic $P2_1/n$ space group; $a = 10.918$ (5) Å, $b = 8.729$ (4) Å, $c = 8.882$ (4) Å, $\beta = 102.90$ (2)°, $Z = 4$, $R = 0.070$, $R_w = 0.103$ for 1433 significant reflections ($F_o > 0.0$) $\{w = 0.3931/[\sigma^2(F_o) + 0.0896F_o^2]\}$.

II: $C_8H_{11}N_3O_2$; monoclinic $P2_1$ space group; $a = 10.924$ (5) Å, $b = 6.493$ (3) Å, $c = 6.013$ (3) Å, $\beta = 97.83$ (2)°, $Z = 2$, $R = 0.046$, $R_w = 0.045$ for 809 significant reflections ($F_o > 0.0$) $\{w = 1.0/[\sigma^2(F_o) + 0.0224F_o^2]\}$.

III: $C_{10}H_{11}N_3O_2$; monoclinic $P2_1/n$ space group; $a = 10.922$ (5) Å, $b = 9.143$ (5) Å, $c = 10.053$ (5) Å, $\beta = 94.05$ (2)°, $Z = 4$, $R = 0.061$, $R_w = 0.086$ for 1737 significant reflections ($F_o > 0.0$) $\{w = 1.0/[\sigma^2(F_o) + 0.0379F_o^2]\}$.

IV: $C_{10}H_{13}N_3O_2$; triclinic $P\bar{1}$ space group; $a = 10.983$ (6) Å, $b = 11.024$ (6) Å, $c = 8.562$ (4) Å, $\alpha = 93.30$ (3), $\beta = 92.09$ (3), $\gamma = 79.32$ (3)°, $Z = 4$ (two crystallographic independent molecules in the asymmetric unit), $R = 0.069$, $R_w = 0.118$ for 3178 significant reflections ($F_o > 0.0$) $\{w = 0.0992/[\sigma^2(F_o) + 0.2636F_o^2]\}$.

V: $C_{10}H_{15}N_3O_2$; orthorhombic $P2_12_12_1$ space group; $a = 11.720$ (6) Å, $b = 10.693$ (5) Å, $c = 8.658$ (4) Å, $Z = 4$, $R = 0.072$, $R_w = 0.081$ for 1113 significant reflections ($F_o > 0.0$) $\{w = 1.0/[\sigma^2(F_o) + 0.1630F_o^2]\}$.

VII: $C_9H_{11}N_3O_2$; monoclinic $P2_1/c$ space group; $a = 6.142$ (3) Å, $b = 12.240$ (6) Å, $c = 12.698$ (6) Å, $\beta = 103.66$ (2)°, $Z = 4$, $R = 0.064$, $R_w = 0.084$ for 1610 significant reflections ($F_o > 0.0$) $\{w = 1.00/[\sigma^2(F_o) + 0.0286F_o^2]\}$.

VIII: $C_{11}H_{14}N_2O_2$; monoclinic $P2_1/n$ space group; $a = 12.052$ (6) Å, $b = 9.828$ (5) Å, $c = 9.243$ (5) Å, $\beta = 90.65$ (2)°, $Z = 4$, $R = 0.095$, $R_w = 0.152$ for 1868 significant reflections ($F_o > 0.0$) $\{w = 0.3264/[\sigma^2(F_o) + 0.0658F_o^2]\}$.

IX: $C_{10}H_{10}N_2O_2$; orthorhombic $Pnma$ space group; $a = 7.831$ (4) Å, $b = 8.334$ (4) Å, $c = 13.731$ (7) Å, $Z = 4$, $R = 0.082$, $R_w = 0.115$ for 808 significant reflections ($F_o > 0.0$) $\{w = 0.6648/[\sigma^2(F_o) + 0.0156F_o^2]\}$.

X: $C_{13}H_{12}N_2O_2$; monoclinic $P2_1/n$ space group; $a = 15.110$ (7) Å, $b = 7.264$ (4) Å, $c = 10.019$ (5) Å, $\beta = 98.07$ (2)°, $Z = 4$, $R = 0.066$, $R_w = 0.077$ for 1537 significant reflections ($F_o > 0.0$) $\{w = 0.4529/[\sigma^2(F_o) + 0.0090F_o^2]\}$.

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XI: $C_{10}H_{12}N_2O_2$; orthorhombic $P2_12_12_1$ space group; a = 13.762 (7) Å, b = 8.638 (4) Å, c = 7.907 (4) Å, Z = 4, R = 0.064, R_w = 0.084 for 965 significant reflections ($F_o > 0.0$) $\{w = 0.4684/[\sigma^2(F_o) + 0.0242F_o^2]\}$.

XII: $C_8H_{12}N_2O_2$; monoclinic $C2/c$ space group; a = 13.032 (6) Å, b = 8.776 (4) Å, c = 9.103 (5) Å, β = 128.74 (2)°, Z = 4, R = 0.062, R_w = 0.089 for 745 significant reflections ($F_o > 0.0$) $\{w = 1.0000/[\sigma^2(F_o) + 0.0686F_o^2]\}$.

XIII: $C_{10}H_{10}N_2O_2$; triclinic $P\bar{1}$ space group; a = 10.727 (5) Å, b = 8.219 (4) Å, c = 5.901 (3) Å, α = 103.22 (3), β = 100.85 (3), γ = 79.49 (3)°, Z = 2, R = 0.076, R_w = 0.108 for 1682 significant reflections ($F_o > 0.0$) $\{w = 0.4754/[\sigma^2(F_o) + 0.0305F_o^2]\}$.

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Registry No. I, 61195-22-0; II, 54168-24-0; III, 102494-19-9; IV, 102494-20-2; V, 102494-21-3; VII, 78790-57-5; VIII, 23292-39-9; IX, 72282-77-0; X, 77762-21-1; XI, 72282-78-1; XII, 3661-10-7; XIII, 23196-38-5; spiro[2.4]hepta-4,6-diene, 765-46-8; 4-methyl-1,2,4-triazoline-3,5-dione, 13274-43-6.

Supplementary Material Available: Listing of observed and calculated structure factors, atomic coordinates, and anisotropic temperature factors (129 pages). Ordering information is given on any current masthead page.

Mechanism of Ketone n → π^* Optical Activity. Experimental and Computed Chiroptical Properties of 4-Axial and 4-Equatorial Alkyladamantan-2-ones[1]

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Abstract: (1*S*,3*R*)-4*S*(a)- and 4*R*(e)-substituted adamantan-2-ones were prepared and their circular dichroism (CD) spectra measured. The substituent groups include methyl, ethyl, isopropyl, *tert*-butyl, neohexyl, and deuterio. The long-wavelength $n \rightarrow \pi^*$ CD transitions of the equatorial alkyladamantanones agree in sign and magnitude with octant rule predictions for *back* octants, while those of the axial isomers agree with predictions based upon front octants. The deuterio ketones exhibit the expected reversed-octant contributions of deuterium located in a back octant for each isomer. Calculations in the random phase approximation (RPA) are analyzed to determine the mechanisms responsible for the rotatory intensity. A μ–m mechanism is extracted from effective bond transition moments, and a set of additive bond increments is displayed that combines features of both the "perturbed chromophore" and "through-bond coupling" models for ketone optical activity. The mechanistic analysis shows octant-consignate coupling contributions, but the nature of the third nodal surface of the octant rule remains an a posteriori construct.

In the nearly 25 years since Moffitt et al.[3] proposed the octant rule for chiral saturated alkyl ketones, it has enjoyed wide application in interpreting details of absolute configuration and conformation from the circular dichroism (CD) or optical rotatory dispersion spectrum. The rule divides all space surrounding the carbonyl chromophore into eight regions (octants), and the octant occupied by a particular atom or group (perturber) determines the sign of its contribution to the rotatory strength of the n → π^* transition. The octants are derived, in part, from the local symmetry (C_{2v}) of the carbonyl group: reflection of a perturber across either of the symmetry planes *XZ* and *YZ* in Figure 1 leads to a mirror image molecular fragment and hence to an oppositely signed contribution to the rotatory strength. The quadrants thus defined are further divided into front and back octants by a third surface supposedly associated with the non-symmetry-determined nodes of the relevant carbonyl n and π^* orbitals.

As originally proposed, the third surface is a plane bisecting the C═O bond (Figure 1, left). More recently, the results from CNDO/S calculations were used to construct a concave third surface (Figure 1, right), in better agreement with experiment.[4-6] In practical applications the contributions from different substituents are assumed to be additive, and Figure 1, middle, shows the sign distribution defined as *consignate*[7] for rotatory strength contributions from alkyl perturbers in the respective octants. Atoms having counterparts symmetrically placed across the carbonyl symmetry planes (*XZ*, *YZ*) and atoms lying in symmetry planes are assumed to make no net contribution to the CD.

In this form the octant rule is simple and straightforward to apply, and has been used in establishing the absolute configuration of a large number of natural products or their derivatives and in

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