and for providing laboratory facilities for the synthesis. We also thank Peter Chen for help with the synthetic work and Albert Cross for many helpful discussions.

Registry No. AA, 53215-63-7; EE, 10184-98-2; AE, 85533-76-2; Trp-Gly, 7360-09-0; NATA, 2382-79-8; NATE, 2382-80-1; NAT, 1218-34-4; Gly-Trp, 2390-74-1; Gly-Trp-Gly, 23067-32-5; Gly-Trp-Lgy-Gly, 24591-52-4; ethyl indole-3-propionic acid, 40641-03-0; tryptophan ethyl ester, 7479-05-2; indole-3-propionamide, 5814-93-7; tryptophanamide, 20696-57-5; indole-3-propionic acid, 830-96-6; tryptophan, 73-22-3; indole-3-carboxaldehyde, 487-89-8; diethyl malonate, 105-53-3; ethyl 2-carbethoxy-3-(3′-indoyl)acrylate, 10184-96-0; ammonia, 7664-41-7; ethyl malonamate, 7597-56-0; 2-carbethoxy-3-(3′-indolyl)acrylamide, 85506-91-8.

Novel Example of Simultaneous Double N-Inversion in the Solid State

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Abstract: Two configurational isomers (endo and exo) of the mono-adduct and one isomer (endo, endo) of the bis-adduct of 11-cyano-1,6-methano[10]annulene with 4-methyl-1,2,4-triazoline-3,5-dione have been isolated and their crystal structures determined by X-ray diffraction methods. The thermodynamically less stable isomer (exo) is transformed to the endo isomer upon heating a solid sample to ca. 175 °C. This process was detected by high-temperature diffraction methods. The change of configuration is explained by a simultaneous double N-inversion with a doubly planar transition state.

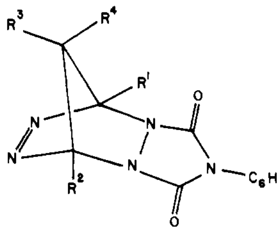
Atomic inversion is one of the most subtle of molecular processes, since only a reversal of configuration results, no bonds are broken, and no other chemical reactant is required.

The subject of atomic inversion was extensively studied in the last 6 decades since the early work of Meisenheimer and co-workers[1] who suggested that an inversion process was responsible for the inability of trivalent nitrogen to sustain optical activity. Thermodynamic data, mainly height of the energy barrier, were determined from experimental methods such as infrared, microwave, and NMR spectroscopy, from studies of the kinetics of decay of optical activity that accompanies racemization, or from theoretical calculations. These various approaches yielded thermodynamic data for over 200 compounds involving inversion of C, N, O, S, or P atoms. However, most of the experiments were carried out on solutions of the compounds. The results have been reviewed by Lambert,[2] Lehn,[3] and others.

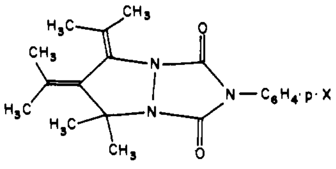
Nitrogen is the most thoroughly studied central atom in the field of atomic inversion. Thorough studies have been made with molecules containing two nitrogen atoms that are singly bonded to each other.[4] Although conformational processes have been observed in some of these molecules, in most of them the process is a rapid consecutive inversion about two nitrogen atoms. A simultaneous inversion about both atoms has been rejected. In cyclic hydrazides in general or in the 1,2,4-triazolidinedione ring in particular, it is generally believed that conjugation of the N-lone pair with a carbonyl group stabilizes planarity at the N atoms, lowering the inversion barrier.[5]

Arnold and co-workers[6] have studied the stereochemistry of the urazole moiety in I by NMR spectroscopy.

The spectra were unchanged over the temperature range +60 to −60 °C. The observations were consistent either with a rigid urazole moiety, where the hydrazine nitrogens are planar or pyramidal, or with one that is rapidly inverting even at −60 °C. variable-temperature NMR studies of related compounds were carried out, leading to the conclusion that the hydrazine nitrogens in the urazole ring do not have rigid, pyramidal structures. The absence of temperature dependence in the spectra also argues against inverting pyramidal conformations for the hydrazine nitrogens. The conclusion was, therefore, that the hydrazine nitrogens in the urazole ring of I must be planar or very close to planar.



I



II a: X = Br b: X = H

Pasto and co-workers[7] have reported results of dynamic nuclear magnetic resonance (DNMR) studies on IIb and the crystal structure of IIa. The molecular structure indicated that the hydrazine nitrogens in the urazole ring are not planar (the interplanar angle is 160.9°). The DNMR studies showed temperature-dependent spectra with coalescence temperature for the dynamic process at −28 °C, which afforded $\Delta G^{\ddagger} = 11.9$ kcal/mol. comparison of the two possible explanations for the change of configuration, enantiomerization of the skewed dienes chromophore or N–N bridge inversion, led to the conclusion that N–N bridge inversion is the phenomenon giving rise to the observed results.

In the course of a study of the configuration of Diels–Alder adducts of propellanes and of bridged[10]annulenes with *N*-methyl- and *N*-phenyltriazolinedione,[8a] the Alder *exo*-III- and *endo*-IV-type isomers of the adducts of 11-cyano-1,6-methano-[10]annulene with 4-methyl-1,2,4-triazoline-3,5-dione[8b] have been isolated and their structures determined by X-ray diffraction

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(1) Meisenheimer, J.; Angerman, C.; Finn, O.; Vieweg, E. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 1744–1759.

(2) Lambert, J. B. *Top. Stereochem.* **1971**, *6*, 19–105.

(3) Lehn, J. M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311–377.

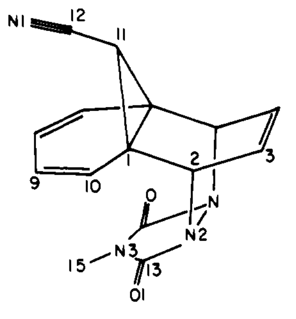
(4) (a) Anderson, J. E.; Lehn, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 81–87. (b) Allred, E. L.; Anderson, C. L.; Miller, R. L.; Johnson, A. L. *Tetrahedron Lett.* **1967**, 525–531. (c) Lehn, J. M.; Wagner, J. *Tetrahedron* **1969**, *25*, 677–689. (d) Wagner, J.; Wojnarowski, W.; Anderson, J. E.; Lehn, J. M. *Ibid.* **1969**, *25*, 657–676. (e) Nelsen, S. F.; Hollinsed, W. C.; Grezzo, L. A.; Parmelee, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 7347–7352.

(5) The calculations were done by MNDO and ab initio STO-3G for suitable models. Arad, D.; Apeloig, Y., to be submitted for publication.

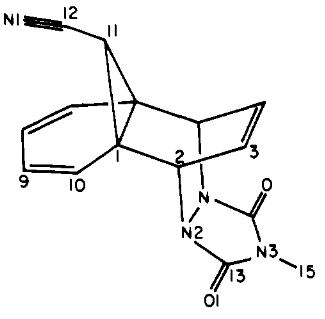
(6) Evning, A. B.; Arnold, D. R.; Karnischky, L. A.; Strom, E. *J. Am. Chem. Soc.* **1970**, *92*, 6218–6231.

(7) Pasto, D. J.; Scheidt, W. R. *J. Org. Chem.* **1975**, *40*, 1444–1447.

(8) (a) Ashkenazi, P.; Kaftory, M.; Ginsburg, D., to be submitted for publication. (b) Ashkenazi, P.; Kaftory, M.; Arad, D.; Apeloig, Y.; Ginsburg, D. *Hel. Chim. Acta* **1981**, *64*, 579–581.

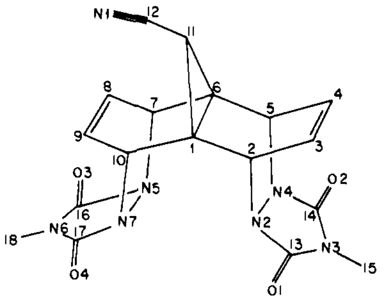


III (exo)



IV (endo)

methods. Treatment of III and IV with another equivalent of 4-methyl-1,2,4-triazoline-3,5-dione resulted in only one isomer of the bis-adduct V (endo–endo) as was shown by X-ray crystal structure.



V

Molecular Structures of III–V

Atomic positions for compounds III–V are given in Tables I–III, respectively. Comparison of bond lengths and angles in the two isomers of the mono-adduct are given in Tables IV and V. Bond lengths and angles in the bis-adduct are given in Tables VI and VII, respectively. Stereoviews[9] of the molecules III–V are shown in Figures 1–3, respectively.

Perhaps the most striking difference between the two isomers is the degree of pyramidality of the hydrazine nitrogen atoms. The angles between the planes described by atoms N2, N2′, C2, C2′[10] and N2, N2′, C13, C13′ are 152.1° in the exo isomer and 137.0° in the endo isomer; the angles observed in the bis-adduct are 131.0 and 133.8°. It should also be noted that there are significant differences between bond lengths and angles, especially in the urazole ring.

Mechanism of the Configurational Change

It was noted above that a single isomer (endo–endo) of the bis-adduct was obtained. This finding suggests that the mono-adduct of the exo-type isomer undergoes configurational change to the endo-type isomer prior to or during the reaction with the second equivalent of the dienophile.[11]

Table I. Exo Isomer III: Atomic Coordinates for Non-Hydrogen Atoms (×10^4) and for Hydrogens (×10^3)[a]

atom	x	y	z	U_{eq}
O(1)	2702 (3)	2614 (6)	10670 (0)	50 (2)
N(1)	5000 (0)	6 (12)	3406 (10)	52 (4)
N(2)	4286 (4)	422 (6)	9883 (8)	34 (2)
N(3)	5000 (0)	3049 (8)	10961 (9)	30 (3)
C(1)	4225 (4)	294 (7)	7254 (8)	26 (2)
C(2)	3725 (5)	−680 (6)	8655 (9)	29 (2)
C(3)	4334 (6)	−2629 (7)	8826 (8)	38 (2)
C(9)	4276 (6)	3513 (7)	6208 (9)	38 (2)
C(10)	3568 (6)	2078 (7)	6783 (8)	33 (3)
C(11)	5000 (0)	−895 (10)	6148 (9)	28 (3)
C(12)	5000 (0)	−377 (10)	4608 (10)	31 (3)
C(13)	3857 (5)	2087 (8)	10503 (8)	34 (3)
C(15)	5000 (0)	4562 (14)	12017 (13)	48 (5)
H(2)	274 (5)	−54 (6)	882 (7)	
H(3)	378 (5)	−389 (7)	900 (6)	
H(9)	377 (8)	477 (11)	590 (11)	
H(10)	275 (6)	217 (8)	697 (7)	
H(11)	500 (0)	−246 (10)	642 (9)	
H(151)	422 (9)	543 (15)	1202 (14)	
H(152)	500 (0)	417 (20)	1298 (19)	

[a] U_{eq} (Å^2 × 10^3) = $^1/_3$ trace $\tilde{U}$.

Table II. Endo Isomer IV: Atomic Coordinates for Non-Hydrogen Atoms (×10^4) and for Hydrogens (×10^3)[a]

atom	x	y	z	U_{eq}
O(1)	8933 (2)	4886 (3)	3667 (3)	70 (2)
N(1)	7260 (3)	2500 (0)	−3101 (3)	51 (2)
N(2)	8760 (2)	3255 (2)	2072 (2)	42 (1)
N(3)	9125 (3)	2500 (0)	3980 (3)	41 (2)
C(1)	8130 (2)	3301 (3)	1 (3)	40 (2)
C(2)	7897 (3)	3831 (3)	1322 (3)	48 (2)
C(3)	6970 (3)	3193 (4)	1859 (4)	69 (2)
C(9)	9571 (3)	3230 (5)	−1393 (3)	73 (2)
C(10)	8946 (3)	3988 (4)	−705 (3)	60 (2)
C(11)	7314 (3)	2500 (0)	−675 (4)	39 (2)
C(12)	7294 (3)	2500 (0)	−2027 (4)	39 (2)
C(13)	8916 (2)	3690 (3)	3298 (3)	45 (2)
C(15)	9430 (5)	2500 (0)	5279 (5)	59 (3)
H(2)	794 (3)	480 (4)	137 (3)	
H(3)	640 (3)	388 (5)	217 (4)	
H(9)	1005 (6)	379 (8)	−196 (7)	
H(10)	896 (3)	493 (5)	−54 (5)	
H(11)	663 (6)	250 (0)	−26 (7)	
H(151)	981 (4)	166 (5)	555 (6)	
H(152)	884 (5)	250 (0)	580 (8)	

[a] U_{eq} (Å × 10^3) = $^1/_3$ trace $\tilde{U}$.

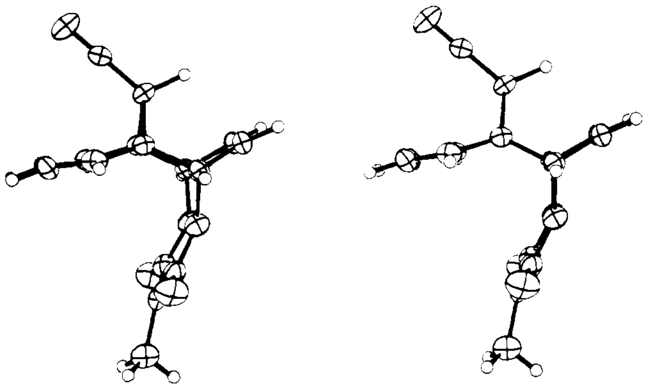


Figure 1. Stereoview of III.

Configurational change, in solution, of Diels–Alder adducts was observed and attributed to the fact that one of the isomers is kinetically more stable and the other thermodynamically more stable. Several mechanisms were proposed[12] for explaining the change of the configuration: retrodiene reaction followed by anti-Alder addition or C–H bond cleavage and shift mechanism with diradical intermediate. Another possible mechanism would be a double N-inversion process. At range of temperatures 25 to −20 °C, ^{1}H and ^{13}C NMR spectra of both isomers in solution were identical, and no coalescence temperature was observed. These observations are consistent either with a rigid urazole moiety where the hydrazine nitrogens are pyramidal and the conformation of the molecule is that of the thermodynamically more stable

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[9] Johnson, C. K. "ORTEP, a Fortran Thermal-Ellipsoid Plots Program for Crystal Structure Illustrations"; ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

[10] The molecules in both isomers possess a crystallographic mirror plane passing through atoms N1, C11, N3, C15. The dashed atoms are, therefore, atoms related by mirror plane symmetry.

[11] The nonappearance of another isomer (endo–exo) of the bis-adduct could not be due to inherent instability as such a bis-adduct was formed from 1,6-methano[10]annulene: Ashkenazi, P.; Kaftory, M.; Ginsburg, D., to be submitted for publication.

[12] Craig, D. *J. Am. Chem. Soc.* **1951**, *73*, 4889–4892.

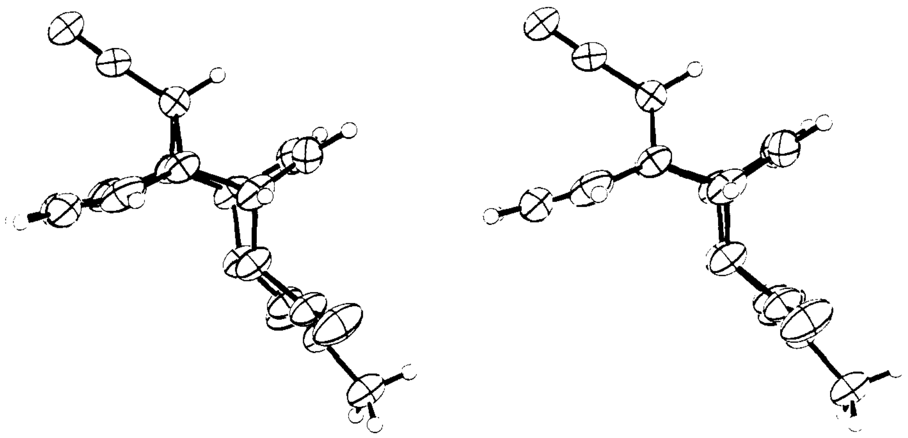

Figure 2. Stereoview of IV.

Table III. Bis-adduct V: Atomic Coordinates for Non-Hydrogen Atoms (×10⁴) and for Hydrogens (×10³)[a]

atom	*x*	*y*	*z*	U_{eq}
O(1)	4209 (4)	1284 (1)	1977 (3)	43 (2)
O(2)	7765 (4)	−174 (1)	975 (3)	56 (2)
O(3)	8395 (5)	672 (1)	−3742 (3)	72 (2)
O(4)	4451 (4)	2078 (1)	−3011 (3)	54 (2)
N(1)	13323 (6)	2616 (2)	−113 (3)	59 (2)
N(2)	6604 (4)	1231 (1)	778 (3)	31 (2)
N(3)	5572 (4)	447 (1)	1517 (3)	37 (2)
N(4)	7768 (4)	773 (1)	498 (3)	32 (2)
N(5)	8102 (4)	1191 (1)	−1955 (3)	37 (2)
N(6)	6009 (5)	1302 (2)	−3643 (3)	48 (2)
N(7)	6851 (4)	1634 (1)	−1712 (3)	33 (2)
C(1)	8840 (5)	1890 (1)	206 (3)	29 (2)
C(2)	7727 (5)	1730 (1)	1268 (3)	31 (2)
C(3)	8953 (5)	1515 (2)	2425 (3)	38 (2)
C(4)	10019 (5)	1084 (2)	2197 (4)	38 (2)
C(5)	9800 (5)	915 (1)	829 (3)	32 (2)
C(6)	10102 (5)	1411 (1)	−32 (3)	29 (2)
C(7)	10060 (5)	1335 (2)	−1463 (3)	34 (2)
C(8)	10404 (5)	1883 (2)	−2097 (3)	37 (2)
C(9)	9266 (5)	2292 (2)	−1880 (3)	35 (2)
C(10)	7867 (5)	2124 (1)	−1049 (4)	32 (2)
C(11)	10910 (5)	1941 (2)	584 (3)	32 (2)
C(12)	12181 (5)	2317 (2)	104 (4)	37 (2)
C(13)	5341 (5)	1020 (2)	1498 (3)	31 (2)
C(14)	7128 (5)	293 (2)	1012 (4)	36 (2)
C(15)	4444 (6)	57 (2)	2142 (4)	54 (2)
C(16)	7613 (6)	1020 (2)	−3198 (4)	44 (2)
C(17)	5641 (6)	1718 (2)	−2822 (4)	41 (2)
C(18)	4938 (9)	1229 (2)	−4926 (5)	82 (3)
O(W)	6838 (14)	4777 (4)	527 (12)	149 (9)
H(2)	687 (4)	202 (1)	147 (3)	
H(3)	894 (4)	167 (1)	325 (3)	
H(4)	1082 (5)	90 (1)	276 (3)	
H(5)	1039 (5)	57 (1)	65 (3)	
H(7)	1087 (4)	103 (1)	−161 (3)	
H(8)	1136 (4)	191 (1)	−261 (3)	
H(9)	921 (5)	265 (2)	−224 (4)	
H(10)	695 (4)	241 (1)	−93 (3)	
H(11)	1131 (4)	193 (1)	140 (3)	
H(151)	476 (7)	6 (2)	296 (5)	
H(152)	272 (10)	16 (3)	203 (8)	
H(153)	458 (9)	−28 (2)	194 (6)	
H(181)	360 (10)	147 (3)	−496 (6)	
H(182)	447 (9)	90 (3)	−489 (6)	
H(183)	573 (10)	132 (3)	−543 (7)	

[a] U_{eq} (Å × 10³) = ⅓ trace $\tilde{U}$.

Table IV. Bond Lengths (Å) in III and IV[a]

	exo-III	*endo*-IV
C(1)–C(13)	1.220 (5)	1.205 (4)
N(1)–C(12)	1.13 (1)	1.148 (5)
N(2)–C(2)	1.470 (9)	1.504 (4)
N(2)–C(13)	1.368 (7)	1.389 (3)
N(3)–C(13)	1.390 (6)	1.375 (3)
N(3)–C(15)	1.43 (1)	1.447 (6)
C(1)–C(2)	1.530 (9)	1.530 (4)
C(1)–C(10)	1.479 (7)	1.476 (4)
C(1)–C(11)	1.520 (8)	1.511 (4)
C(2)–C(3)	1.507 (6)	1.492 (5)
C(9)–C(10)	1.338 (8)	1.324 (5)
C(11)–C(12)	1.45 (1)	1.445 (6)
N(2)–N(2)′	1.426 (5)	1.436 (2)
C(1)–C(1)′	1.547 (5)	1.525 (4)
C(3)–C(3)′	1.329 (8)	1.318 (5)
C(9)–C(9)′	1.444 (8)	1.390 (6)

[a] Estimated standard deviations are given in parentheses (C–H bond lengths lie in the range 0.84–1.05 Å).

Table V. Bond Angles (deg) in III and IV

	exo-III	*endo*-IV
C(2)–N(2)–C(13)	130.2 (4)	120.5 (2)
C(13)–N(3)–C(15)	124.2 (3)	124.4 (1)
C(2)–C(1)–C(10)	118.5 (4)	118.3 (2)
C(2)–C(1)–C(11)	118.1 (4)	117.5 (2)
C(10)–C(1)–C(11)	120.0 (6)	120.6 (2)
N(2)–C(2)–C(1)	105.8 (4)	102.5 (2)
N(2)–C(2)–C(3)	104.3 (5)	106.2 (2)
C(1)–C(2)–C(3)	111.2 (5)	112.8 (2)
C(1)–C(10)–C(9)	121.3 (5)	120.4 (3)
C(1)–C(11)–C(12)	120.1 (5)	119.4 (2)
N(1)–C(12)–C(11)	179.2 (8)	178.8 (4)
O(1)–C(13)–N(2)	127.3 (5)	126.4 (2)
O(1)–C(13)–N(3)	126.1 (5)	127.0 (3)
N(2)–C(13)–N(3)	106.5 (4)	106.5 (2)
C(2)–N(2)–N(2)′	112.3 (5)	111.4 (2)
C(13)–N(2)–N(2)′	108.2 (4)	107.4 (1)
C(13)–N(3)–C(13)′	110.3 (5)	110.9 (2)
C(2)–C(1)–C(1)′	109.0 (4)	109.2 (2)
C(10)–C(1)–C(1)′	116.3 (4)	116.3 (2)
C(11)–C(1)–C(1)′	59.4 (3)	59.7 (1)
C(2)–C(3)–C(3)′	113.8 (4)	114.0 (3)
C(10)–C(9)–C(9)′	121.9 (5)	123.0 (3)
C(1)–C(11)–C(1)′	61.2 (3)	60.6 (2)

isomer (endo) or with one that is rapidly flipping even at −20 °C. We would suggest a check of Arnold's[6] arguments against an inversion process and his conclusion that the hydrazine nitrogens in I must be planar or very close to planar. The crystal structures of a large number of compounds possessing a 4-substituted-1,2,4-triazolidine-3,5-dione moiety, elucidated by X-ray diffraction methods, indicate that in all cases the nitrogen atoms are pyramidal.

Attempts to recrystallize the less stable *exo* isomer by dissolving either the exo or endo solid materials in various solvents failed: all attempts afforded crystals of the endo isomer.

Theoretical calculations[5] established that the endo isomer is more stable than the exo isomer by ca. 2 kcal/mol. Such a difference means that at ambient temperature the equilibrium is

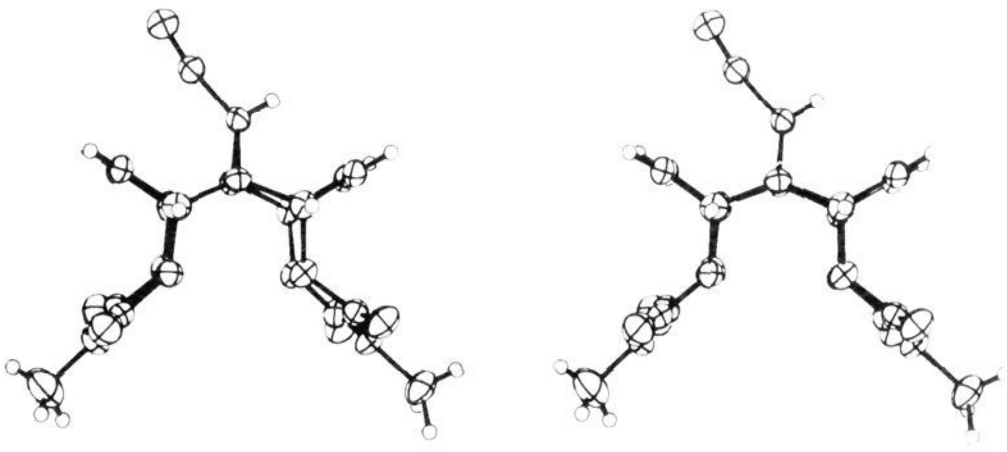

Figure 3. Stereoview of V.

Table VI. Bond Lengths (Å) in V[a]

O(1)–C(13)	1.210 (5)	N(6)–C(18)	1.471 (6)
O(2)–C(14)	1.208 (5)	N(7)–C(10)	1.504 (3)
O(3)–C(16)	1.205 (5)	N(7)–C(17)	1.386 (4)
O(4)–C(17)	1.217 (5)	C(1)–C(2)	1.536 (5)
N(1)–C(12)	1.145 (6)	C(1)–C(6)	1.510 (4)
N(2)–N(4)	1.441 (3)	C(1)–C(10)	1.529 (4)
N(2)–C(2)	1.495 (3)	C(1)–C(11)	1.512 (5)
N(2)–C(13)	1.379 (4)	C(2)–C(3)	1.506 (4)
N(3)–C(13)	1.376 (5)	C(3)–C(4)	1.333 (6)
N(3)–C(14)	1.377 (5)	C(4)–C(5)	1.501 (5)
N(3)–C(15)	1.466 (5)	C(5)–C(6)	1.534 (4)
N(4)–C(5)	1.512 (4)	C(6)–C(7)	1.535 (4)
N(4)–C(14)	1.381 (5)	C(6)–C(11)	1.503 (5)
N(5)–N(7)	1.445 (3)	C(7)–C(8)	1.508 (6)
N(5)–C(7)	1.490 (4)	C(8)–C(9)	1.323 (6)
N(5)–C(16)	1.383 (5)	C(9)–C(10)	1.501 (5)
N(6)–C(16)	1.374 (5)	C(11)–C(12)	1.438 (6)
N(6)–C(17)	1.376 (6)		

[a] C–H bond lengths lie in the range 0.85–1.27 Å).

Table VII. Bond Angles in V

N(4)–N(2)–C(2)	111.4 (2)	C(4)–C(5)–C(6)	111.9 (2)
N(4)–N(2)–C(13)	107.5 (2)	C(1)–C(6)–C(5)	109.7 (2)
O(2)–N(2)–C(13)	118.2 (2)	C(1)–C(6)–C(7)	109.4 (2)
C(13)–N(3)–C(14)	111.4 (3)	C(1)–C(6)–C(11)	60.2 (2)
C(13)–N(3)–C(15)	124.1 (2)	C(5)–C(6)–C(7)	121.5 (2)
C(14)–N(3)–C(15)	124.1 (3)	C(5)–C(6)–C(11)	117.8 (2)
N(2)–N(4)–C(5)	111.8 (2)	C(7)–C(6)–C(11)	119.0 (2)
N(2)–N(4)–C(14)	107.6 (2)	N(5)–C(7)–C(6)	104.9 (2)
C(5)–N(4)–C(14)	118.0 (2)	N(5)–C(7)–C(8)	104.8 (3)
N(7)–N(5)–C(7)	111.5 (2)	C(6)–C(7)–C(8)	111.4 (3)
N(7)–N(5)–C(16)	107.8 (3)	C(7)–C(8)–C(9)	114.1 (3)
C(7)–N(5)–C(16)	120.4 (2)	C(8)–C(9)–C(10)	114.0 (3)
C(16)–N(6)–C(17)	111.4 (3)	N(7)–C(10)–C(1)	105.2 (2)
C(16)–N(6)–C(18)	123.8 (3)	N(7)–C(10)–C(9)	105.1 (3)
C(17)–N(6)–C(18)	124.0 (4)	C(1)–C(10)–C(9)	110.3 (3)
N(5)–N(7)–C(10)	111.7 (2)	C(1)–C(11)–C(6)	60.1 (2)
N(5)–N(7)–C(17)	107.0 (2)	C(1)–C(11)–C(12)	128.9 (3)
C(10)–N(7)–C(17)	120.0 (2)	C(6)–C(11)–C(12)	126.8 (3)
C(2)–C(1)–C(6)	109.9 (2)	N(1)–C(12)–C(11)	170.6 (4)
C(2)–C(1)–C(10)	120.6 (3)	O(1)–C(13)–N(2)	126.8 (4)
C(2)–C(1)–C(11)	116.0 (2)	O(1)–C(13)–N(3)	126.8 (3)
C(6)–C(1)–C(10)	110.2 (2)	N(2)–C(13)–N(3)	106.3 (2)
C(6)–C(1)–C(11)	59.7 (2)	O(2)–C(14)–N(3)	127.0 (3)
C(10)–C(1)–C(11)	121.6 (2)	O(2)–C(14)–N(4)	126.6 (3)
N(2)–C(2)–C(1)	105.1 (2)	N(3)–C(14)–N(4)	106.3 (3)
N(2)–C(2)–C(3)	104.3 (2)	O(3)–C(16)–N(5)	126.3 (4)
O(1)–C(2)–C(3)	112.0 (2)	O(3)–C(16)–N(6)	127.5 (4)
C(2)–C(3)–C(4)	114.0 (3)	N(5)–C(16)–N(6)	106.1 (3)
C(3)–C(4)–C(5)	113.7 (3)	O(4)–C(17)–N(6)	127.1 (4)
N(4)–C(5)–C(4)	104.4 (2)	O(4)–C(17)–N(7)	126.4 (3)
N(4)–C(5)–C(6)	104.7 (2)	N(6)–C(17)–N(7)	106.4 (3)

shifted to the endo isomer. Lowering the temperature would decrease the amount of the thermodynamically less stable exo isomer, and this would not be detected by NMR spectra.

The thermal behavior of a single crystal of the exo isomer was studied by using a microscope with polarized light. At ca. 75 °C, thin dark lines were observed on the crystal surface followed by intergrowth starting from various points in the crystal that was propagated throughout the crystal, but the crystal's external appearance remained unchanged. There was no indication of sublimation. In order to establish the nature of this change, X-ray powder diffraction patterns of both isomers at room temperature and that of the exo isomer after heating to ca. 180 °C were taken. The diffraction patterns suggested that the exo isomer was transformed to the endo isomer at ca. 175 °C. The powder diffraction patterns taken with HTXRD[13] (high temperature X-ray diffraction) camera is shown in Figure 4. The diffraction pattern of the exo isomer after heating to ca. 180 °C is identical with that of the endo isomer. It should be noted that no impurities were detected, suggesting that no side reaction took place. Figure 5 shows an oscillation photograph of a single crystal of the exo isomer at room temperature. The camera slits were then closed to 1-mm width, and the diffraction pattern was recorded while the crystal was heated to ca. 180 °C. The slits were then reopened, and a second oscillation photograph was taken. The results indicate that the single crystal of the exo isomer turns into polycrystals of the endo isomer.

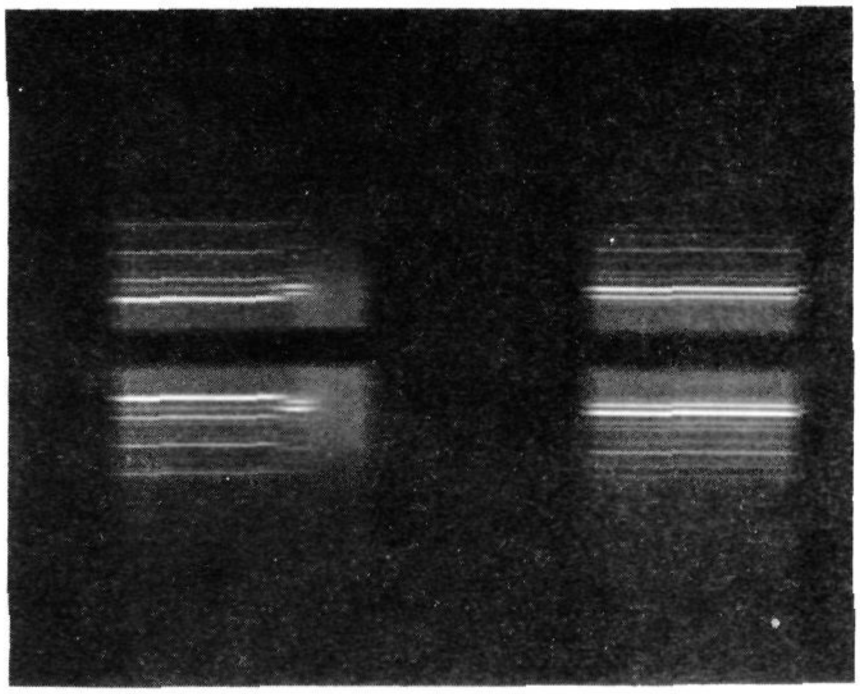

Figure 4. HTXRD patterns: (left) powder of exo isomer (III) during heating from 25 °C to melt 195 °C; (heating rate 1 °C/min); (right) powder of endo isomer (IV) at room temperature.

Comparing the possible mechanisms that were studied in solution such as retro-Diels–Alder-type mechanism and N–N bridge inversion led to the conclusion that the latter mechanism is more acceptable; the retro-Diels–Alder barrier for the isomerization in the adduct between cyclopentadiene and maleic anhydride[14] was found to be 37.5 kcal/mol. As a C–N bond is only slightly weaker than a C–C bond, this barrier for III will not be less than 30 kcal/mol. However the barrier for double N-inversion[5,8b] is calculated to be ca. 7 kcal/mol for the inversion of III to IV and ca. 9 kcal/mol for the inversion from IV to III. The experimental

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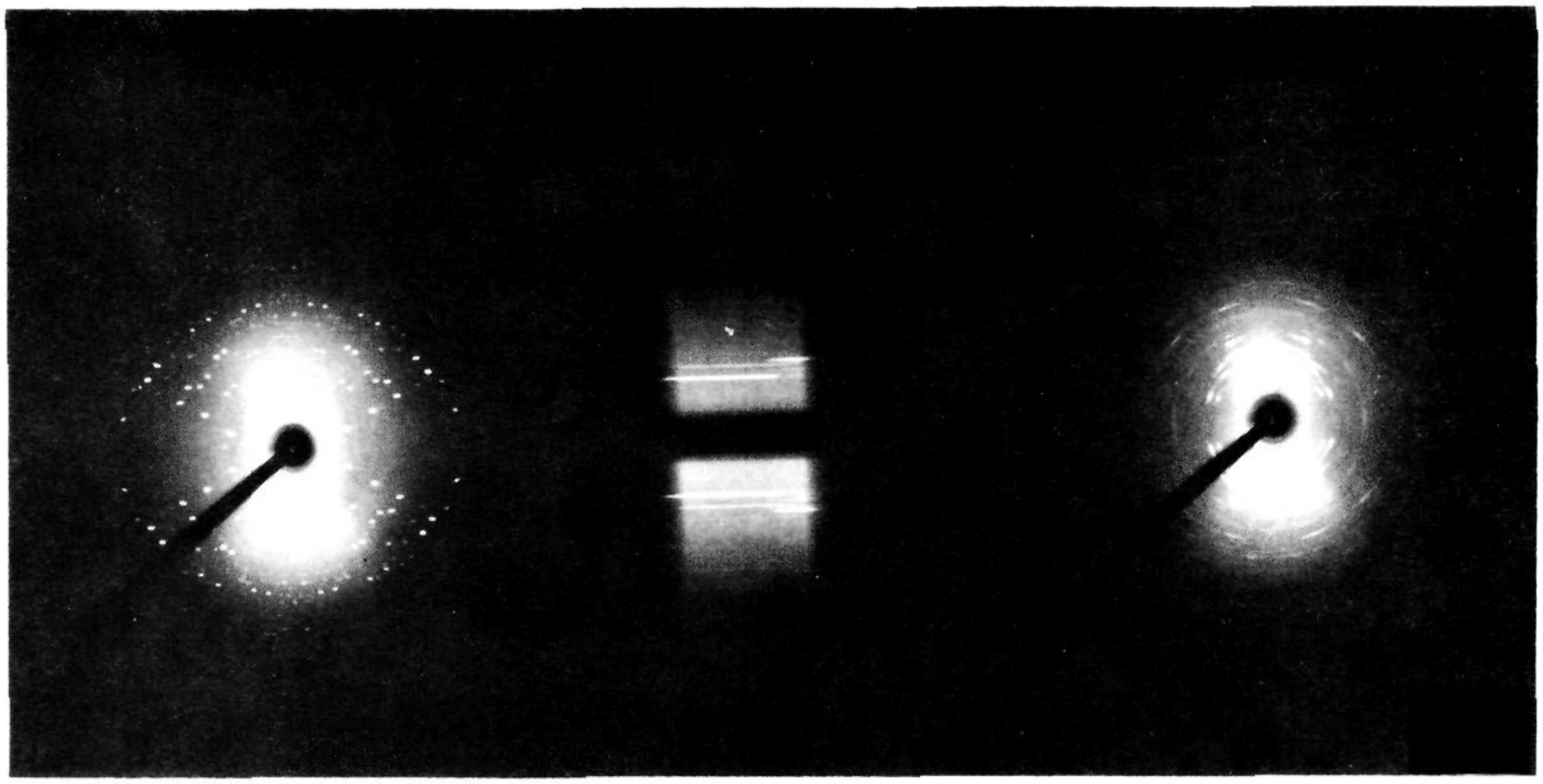

Figure 5. HTXRD patterns of a single crystal of the exo isomer (III); (left) oscillation photograph at room temperature; (middle) recording of the zero layer line (slits at 1-mm width) during heating to ca. 180 °C; (right) oscillation photograph at ca. 180 °C.

barrier for double N-inversion of IIb was found to be 11.9 kcal/mol.[7]

Comparison of the geometrical parameters of the two isomers also supports the N–N bridge inversion mechanism. The less stable exo isomer is expected to be closer to the planar transition state; the angle between the two planes intersecting at the N–N bond is therefore larger (152.1°) than in the endo isomer (137.0°). All the bond lengths involving the hydrazide nitrogen atoms are shorter in the exo isomer (N2–N2′ = 1.425 < 1.436 Å, N2–C2 = 1.470 < 1.504 Å, N2–C13 = 1.367 < 1.389 Å), indicating that those bonds tend to strengthen (inversion process) rather than to weaken (retro-Diels–Alder process). The shortening of the bond between a hydrazide nitrogen atom to the carbonyl carbon atom in the exo isomer also supports the assumption of a planar transition state that is stabilized by conjugation with the carbonyl groups hence lowering the barrier for the inversion.

Conclusions

This is a novel first example of a simultaneous double N-inversion in the solid state. An extensive study is now being carried out attempting to map the inversion pathway using geometrical data obtained by crystal structure elucidation of related compounds and to estimate the structure of such systems near the transition state.

Experimental Section

Intensity data were measured with PW 1100 four-circle computer-controlled diffractometer. The crystal structures were solved by MULTAN 77[15] and refined by SHELX[16] with anisotropic vibrational parametes 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[17] and for H from Stewart et al.[18]

Exo isomer (III): $C_{15}H_{11}N_4O_2$; crystallizes from chloroform as colorless transparent plates, in orthorhombic *Pmn*2$_1$ space group, a = 9.979 (5) Å, b = 7.031 (4) Å, c = 9.094 (5) Å, Z = 2, R = 0.058, R_w = 0.060 for 632 reflections. The molecule possesses a crystallographic mirror plane.

Endo isomer (IV): $C_{15}H_{11}N_4O_2$; crystallizes from ethyl acetate as pale yellowish prisms, in orthorhombic *Pnma* space group, a = 13.318 (7) Å, b = 9.516 (5) Å, c = 10.683 (6) Å, Z = 4, R = 0.064, R_w = 0.088 for 1045 observed reflections. The molecules possesses a crystallographic mirror plane.

Bis-adduct (V): $C_{18}H_{14}N_7O_4\cdot{}^1/_2H_2O$ crystallizes from ethanol as colorless prisms in monoclinic $P2_1/n$ space group, a = 7.303 (4) Å, b = 23.827 (10) Å, c = 10.681 (6) Å, β = 98.37 (2)°, Z = 4, R = 0.071, R_w = 0.069 for 2346 observed reflections. The compound crystallizes with water molecules, which were found to be disordered. The oxygen atom of the water molecule is situated 50% between two carbonyl O atoms of molecules which are related by an *n* glide symmetry operation. The nonbonded distances OW···O3 are 2.849 and 2.941 Å, suggesting a weak hydrogen bond; however, the water H atoms could not be located from a Fourier difference map to support this argument.

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Registry No. III, 77943-77-2; IV, 77888-08-5; V, 77888-09-6; V·$^1/_2H_2O$, 85317-06-2.

Supplementary Material Available: Listing of observed and calculated structure factors and anisotropic thermal parameters (27 pages). Ordering information is given on any current masthead page.

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