bonds (Jeffrey & Maluszynska, 1981). The intermolecular N—H···O hydrogen bonds link molecules related by centres of inversion, effectively resulting in a dimerization of the sulphapyridine molecules. One of the sulphonyl oxygens, O(2), is seen to accept two hydrogen bonds which, perhaps, explains the longer S—O bond length involving this O atom (Cotton & Stokley, 1970). The geometries of the hydrogen bonds are in Table 2.

References

ALLÉAUME, M., GULKO, A., HERBSTEIN, F. H., KAPON, M. & MARSH, R. E. (1976). Acta Cryst. B32, 669–682.

BASAK, A. K., MAZUMDAR, S. K. & CHAUDHURI, S. (1982). Cryst. Struct. Commun. 11, 1609–1616.

BASAK, A. K., MAZUMDAR, S. K. & CHAUDHURI, S. (1983). Acta Cryst. C39, 492–494.

BASAK, A. K., MAZUMDAR, S. K. & CHAUDHURI, S. (1984). Acta Cryst. C40, 419–422.

BOURNE, P. E. & TAYLOR, M. R. (1983). Acta Cryst. C39, 266–268.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

CHANDRASEKHAR, K. (1977). Acta Cryst. B33, 143–145.

COTTON, F. A. & STOKLEY, P. F. (1970). J. Am. Chem. Soc. 92, 294–302.

CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104–109.

DECLERCQ, J.-P., SCHANCK, A., GERMAIN, G., DEREPPE, J. M. & VAN MEERSSCHE, M. (1977). Acta Cryst. B33, 3876–3877.

DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). Acta Cryst. B31, 221–234.

ELIOPOULOUS, E., SHELDRICK, B. & HOMODRAKAS, S. (1983). Acta Cryst. C39, 743–745.

GERMAIN, G., DECLERCQ, J.-P., SCHANCK, A., DEREPPE, J. M. & VAN MEERSSCHE, M. (1977). Acta Cryst. B33, 3878–3880.

HAMILTON, W. C. (1959). Acta Cryst. 12, 609–610.

International Tables for X-ray Crystallography (1974). Vol IV. Birmingham: Kynoch Press.

JEFFREY, G. A. & MALUSZYNSKA, H. (1981). Int. J. Quantum Chem. Quantum Biol. Symp. 8, 231–239.

KÁLMÁN, A., CZUGLER, M. & ARGAY, GY. (1981). Acta Cryst. B37, 868–877.

KRAJEWSKI, J., URBANCZYK-LIPKOWSKA, Z. & GLUZINSKI, P. (1977). Acta Cryst. B33, 2967–2969.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

NITYA ANAND (1979). Burger's Medicinal Chemistry, Part II, edited by M. E. WOLFF, pp. i–40. New York: John Wiley.

SØRENSEN, G. O., MAHLER, L. & RASTRUP-ANDERSON, N. (1974). J. Mol. Struct. 20, 119–126.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

rel-(5R,6R,9S,10S)-5,6,7,8,9,10-Hexahydro-2-phenyl-5,10:6,9-dimethano-1H-[1,2,4]triazolo[1,2-b]phthalazine-1,3(2H)-dione, $C_{18}H_{17}N_3O_2$

BY RAM P. KASHYAP,* WILLIAM H. WATSON, CHENGJIU WU AND PAUL D. BARTLETT

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Abstract. $M_r = 307.33$, monoclinic, $P2_1/n$, $a = 9.439$ (2), $b = 19.454$ (8), $c = 8.382$ (3) Å, $\beta = 102.70$ (2)°, $V = 1501.4$ (9) Å^3, $Z = 4$, $D_x = 1.360$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 7.46$ cm^{-1}, $F(000) = 648$, room temperature, $R = 0.035$ for 1762 unique reflections with $I > 3\sigma(I)$. The central double bond in the anti-sesquinorbornene moiety is 1.327 (3) Å, and the C atoms are slightly pyramidalized. The pyramidalization leads to a 4.3 (4)° deviation from planarity. The phenyl group is planar, the five-membered triazolo ring has an envelope conformation.

Introduction. Although isodicyclopentadiene (1) prefers endo-face attack by many dienophiles to give Diels–Alder cycloadducts with the syn-sesquinorbornene ring system (Sugimoto, Kobuke & Furukawa, 1976; Böhm, Carr, Gleiter & Paquette, 1980; Watson, Galloy, Bartlett & Roof, 1981), it is now found that the stereo course is reversed when more reactive dienophiles are used (Watson, Kashyap, Bartlett & Wu, 1984). To determine whether steric bulkiness or inherent reactivity governs the exo attack, the reaction of (1) with 4-phenyl-3H-triazole-3,5(4H)-dione (PTAD), (2), was studied. The reaction gave the single product (3) in good yield; however, the instability of (3) in solution prevented further chemical characterization. The present study demonstrates that the dienophile attacks from the exo face of the diene to form an anti-type cycloadduct. The structural data permit a comparison of contrasting theoretical approaches and yield parameters needed for the development of molecular mechanical computations on strained bicyclic systems.

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$C_{18}H_{17}N_3O_2$

The reaction of (1) with a similar dienophile, 4-methyl-3H-triazole-3,5(4H)-dione (MTAD) (4), has been reported (Paquette, Carr, Charumilind & Blount, 1980). The cycloadduct was assigned the *syn*-sesquinorbornene structure (5) based upon chemical evidence; however, the ^{13}C and ^1H NMR data appear to be consistent with an *anti*-sesquinorbornene formulation.

(1)　　(2)

(3)　　(4)

(5)
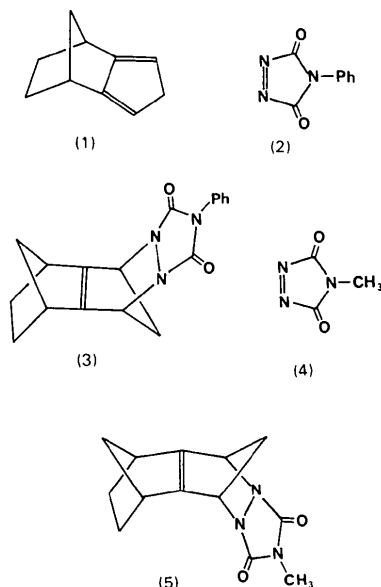
Experimental. Prismatic crystal, $0.45 \times 0.37 \times 0.30$ mm, Syntex $P2_1$ diffractometer, θ–2θ scan, variable scan rate, $2\theta_{max} = 120°$, graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from least squares on 15 medium-angle reflections with angles measured by centering routine associated with the diffractometer system (systematic absences $h+l = 2n+1$ for $h0l$ and $k = 2n+1$ for $0k0$); monitored reflection showed no significant change in intensity; 2051 independent reflections ($0 \leq h \leq 10$, $0 \leq k \leq 20$, $-9 \leq l \leq 8$), 1762 with $I > 3\sigma(I)$; Lorentz and polarization corrections, no absorption correction; direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located all heavy atoms; H atoms located in difference Fourier map but not refined, full-matrix least-squares anisotropic refinement; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$; 208 parameters refined, final $R = 0.035$, $R_w = 0.050$, $S = 2.55$, $(\Delta/\sigma)_{av} = 0.08$, $(\Delta/\sigma)_{max} = 0.12$, highest peak in difference Fourier map 0.16 e Å^{-3}; after final refinement C–H distances adjusted to 1.08 Å for better estimates of inter- and intramolecular contacts; *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) for all computations; atomic scattering factors for C, O, and N from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Table 1 lists atomic positional parameters and U_{eq} values while Table 2 gives bond lengths and valence angles.*

Discussion. Fig. 1 is an *ORTEP* (Johnson, 1971) drawing of the title compound. The molecule is an *anti*-sesquinorbornene with an *endo*-oriented PTAD group. The most notable feature is the nonplanarity of the π-electron system associated with the C(8)–C(9) double bond. While the C(8)–C(9) distance is normal, 1.327 (3) Å, and the C(7)C(8)C(9)C(1) and C(13)-C(8)C(9)C(10) torsion angles are zero as expected [0.1 (4)°], the C(1)C(9)C(8)C(13) and C(7)C(8)C(9)-C(10) torsion angles are 175.9 (4) and -175.6 (4)° indicating a bending of 4.3 (4)° along the C(8)–C(9) axis.

Because of angle deformation about the central double bond, the strain energy in sesquinorbornenes is quite large. This leads to a low out-of-plane bending-force constant (Houk, Rondan, Brown, Jorgensen, Madura & Spellmeyer, 1983), and an asymmetric interaction with the π system can lead to a nonplanar ground-state conformation. In *syn*-sesquinorbornenes the environment is inherently asymmetric, and the central C atoms are pyramidalized leading to deviations from planarity of 18 to 22° (Watson, Galloy, Bartlett & Roof, 1981; Pinkerton, Schwarzenbach, Stibbard, Carrupt & Vogel, 1981; Watson, Galloy, Grossie, Bartlett & Combs, 1984). In *anti*-sesquinorbornenes the environment is more symmetric and smaller deviations from planarity are observed (Watson, Galloy, Bartlett & Roof, 1981; Watson, Kashyap, Bartlett & Wu, 1984; Ermer & Bodecker, 1983).

The driving force for pyramidalization has been attributed to ground-state torsional effects, involving primarily C(1)–H(1)$\cdots$C(9)–C(10) types of interactions (Houk, 1983), antihyperconjugative interactions between π and 'cyclopentane ribbon' orbitals (Gleiter & Spanget-Larsen, 1982; Spanget-Larsen & Gleiter, 1983), or to antihyperconjugative interactions between C(10)–C(11)-type bonds and the π system (Hagenbuch, Vogel, Pinkerton & Schwarzenbach, 1981). In *anti*-sesquinorbornene the forces in the two halves of the molecule are in opposition, and the π system is planar (Watson & Kashyap, unpublished results; *anti*-sesquinorbornene lies on a center of symmetry and must be planar); however, molecular mechanics calculations suggest a bent conformation is lower in energy (Houk *et al.*, 1983; Ermer & Bodecker, 1983).

Compounds such as (3) are of interest as test systems. If half of the sesquinorbornene molecule is perturbed, the effects can be compared with the

Table 1. *Atomic positional parameters* (×10⁴) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

$$U_{eq} = \tfrac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha].$$

	x	y	z	U_{eq}
C(1)	5702 (2)	5880 (1)	4345 (2)	45 (1)
N(2)	4089 (2)	5738 (1)	3726 (2)	42 (1)
C(3)	3616 (2)	5457 (1)	2174 (2)	42 (1)
N(4)	2544 (2)	5896 (1)	1328 (2)	43 (1)
C(5)	2527 (2)	6509 (1)	2192 (2)	43 (1)
N(6)	3394 (2)	6406 (1)	3732 (2)	42 (1)
C(7)	4636 (2)	6905 (1)	4350 (2)	44 (1)
C(8)	5502 (2)	6922 (1)	3052 (2)	42 (1)
C(9)	6141 (2)	6315 (1)	3042 (2)	42 (1)
C(10)	7109 (2)	6347 (1)	1828 (2)	48 (1)
C(11)	8371 (2)	6835 (1)	2633 (3)	57 (1)
C(12)	7624 (2)	7537 (1)	2646 (3)	56 (1)
C(13)	6010 (2)	7386 (1)	1848 (3)	48 (1)
C(14)	6202 (3)	6846 (1)	580 (3)	56 (1)
C(15)	5576 (2)	6430 (1)	5622 (2)	53 (1)
C(16)	1709 (2)	5788 (1)	−302 (2)	45 (1)
C(17)	213 (2)	5841 (1)	−573 (3)	58 (1)
C(18)	−609 (3)	5767 (1)	−2150 (4)	73 (1)
C(19)	66 (3)	5639 (1)	−3420 (3)	73 (2)
C(20)	1545 (3)	5582 (1)	−3131 (3)	68 (1)
C(21)	2392 (2)	5653 (1)	−1559 (3)	53 (1)
O(22)	4011 (2)	4920 (1)	1699 (2)	55 (1)
O(23)	1850 (2)	7024 (1)	1701 (2)	55 (1)

Table 2. *Interatomic distances* (Å) *and valence angles* (°) *with their e.s.d.'s in parentheses*

C(1)–N(2)	1·522 (3)	C(8)–C(9)	1·327 (3)
C(1)–C(9)	1·510 (3)	C(8)–C(13)	1·509 (3)
C(1)–C(15)	1·536 (3)	C(9)–C(10)	1·511 (3)
N(2)–C(3)	1·391 (2)	C(10)–C(11)	1·556 (3)
N(2)–N(6)	1·456 (3)	C(10)–C(14)	1·541 (3)
C(3)–N(4)	1·393 (2)	C(11)–C(12)	1·538 (3)
C(3)–O(22)	1·206 (3)	C(12)–C(13)	1·551 (3)
N(4)–C(5)	1·397 (3)	C(13)–C(14)	1·533 (3)
N(4)–C(16)	1·435 (2)	C(16)–C(17)	1·384 (3)
C(5)–N(6)	1·383 (2)	C(16)–C(21)	1·376 (3)
C(5)–O(23)	1·211 (3)	C(17)–C(18)	1·385 (4)
N(6)–C(7)	1·523 (3)	C(18)–C(19)	1·378 (5)
C(7)–C(8)	1·498 (3)	C(19)–C(20)	1·368 (4)
C(7)–C(15)	1·537 (2)	C(20)–C(21)	1·390 (3)
N(2)C(1)C(9)	105·6 (1)	C(1)C(9)C(8)	107·3 (2)
N(2)C(1)C(15)	98·0 (1)	C(1)C(9)C(10)	144·4 (2)
C(9)C(1)C(15)	100·9 (2)	C(8)C(9)C(10)	108·1 (2)
C(1)N(2)C(3)	118·8 (2)	C(9)C(10)C(11)	104·6 (2)
C(1)N(2)N(6)	104·7 (1)	C(9)C(10)C(14)	98·9 (2)
C(3)N(2)N(6)	107·6 (1)	C(11)C(10)C(14)	99·7 (2)
N(2)C(3)N(4)	106·4 (2)	C(10)C(11)C(12)	103·7 (1)
N(2)C(3)O(22)	126·2 (2)	C(11)C(12)C(13)	103·7 (1)
N(4)C(3)O(22)	127·3 (2)	C(8)C(13)C(12)	104·6 (2)
C(3)N(4)C(5)	110·4 (1)	C(8)C(13)C(14)	99·0 (2)
C(3)N(4)C(16)	125·5 (2)	C(12)C(13)C(14)	100·0 (2)
C(5)N(4)C(16)	123·5 (2)	C(10)C(14)C(13)	95·4 (2)
N(4)C(5)N(6)	106·8 (2)	C(1)C(15)C(7)	93·3 (1)
N(4)C(5)O(23)	126·5 (2)	N(4)C(16)C(17)	118·2 (2)
N(6)C(5)O(23)	126·7 (2)	N(4)C(16)C(21)	120·4 (2)
N(2)N(6)C(5)	107·5 (2)	C(17)C(16)C(21)	121·4 (2)
N(2)N(6)C(7)	104·9 (2)	C(16)C(17)C(18)	119·1 (2)
C(5)N(6)C(7)	118·6 (2)	C(17)C(18)C(19)	119·9 (2)
N(6)C(7)C(8)	105·6 (1)	C(18)C(19)C(20)	120·3 (2)
N(6)C(7)C(15)	97·9 (1)	C(19)C(20)C(21)	120·8 (3)
C(8)C(7)C(15)	101·1 (1)	C(16)C(21)C(20)	118·4 (2)
C(7)C(8)C(9)	107·8 (2)		
C(7)C(8)C(13)	143·5 (2)		
C(9)C(8)C(13)	108·5 (2)		

unperturbed half. The N(2)–N(6) distance of 1·456 (3) Å is significantly shorter than the C(11)–C(12) distance of 1·538 (3) Å which, through accommodation by the bridgehead H atoms, leads to differing torsional interactions. The torsional theory predicts that the molecule should be bent in a direction opposite to that observed. Molecular mechanics calculations (*MM2*, Allinger & Yuh, 1980) in which the N(4) phenyl ring is replaced by an H atom lead to two low-energy conformations. In one conformation the π system is bent by 20–25° in the experimentally observed direction. The second conformation is lower in energy by more than 10·5 kJ mol⁻¹, and the molecule is bent by 10° in the direction predicted for the minimization of torsional effects. The exact values for these distortions depend upon the force-field parameters assigned to atoms N(2) through N(6); however, qualitatively the results are independent of any reasonable values assigned to these parameters.

The observed conformation is not consistent with the torsional-theory predictions. Packing interactions may be of importance or factors such as σ–π interactions might be dominant. The studies of Spanget-Larsen & Gleiter (1983) predict that the extended π-orbital lobes in *syn*-sesquinorbornene will be bent away from the center of the molecule. Preliminary low-temperature X-ray studies of a *syn*-sesquinorbornene derivative show the electron density to be extended as predicted but to be concentrated toward the center of the molecule (Watson, Cromer & Ryan, unpublished results).* While several authors claim to have identified

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* Independent low-temperature studies on crystals grown from different solvent systems yielded the same results. These unexpected observations are being checked by collection of a more extended data set and by investigation of related systems.
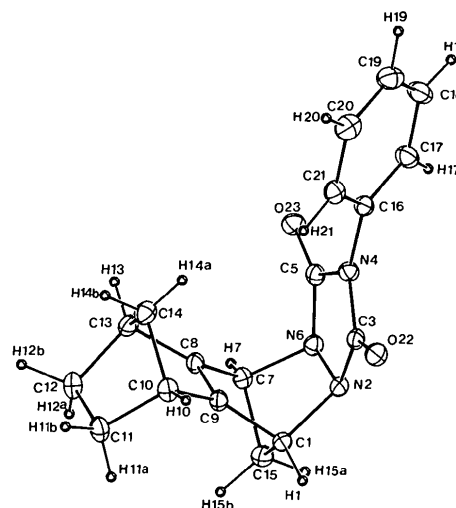

Fig. 1. *ORTEP* drawing of compound (3). Thermal ellipsoids are drawn at the 35% probability level.

conclusively the source of π-orbital distortion, experimental inconsistencies remain.

The phenyl group in (3) is planar and is rotated by 19° from a noncrystallographic mirror plane passing through the molecule. Equivalent distances and angles are internally consistent. The five-membered triazolo ring is in an envelope conformation. The closest intramolecular contacts of significance are H(11b)···H(14b), H(12b)···H(14b) and H(14a)···H(21) of 2·62, 2·65 and 2·59 Å. There are seven intermolecular contacts between 2·32 and 2·60 Å.

References

ALLINGER, N. L. & YUH, Y. H. (1980). *Molecular Mechanics, MM2. Quantum Chem. Program Exch.* No. 395.

BÖHM, M. C., CARR, R. V. C., GLEITER, R. & PAQUETTE, L. A. (1980). *J. Am. Chem. Soc.* **102**, 7218–7228.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

ERMER, O. & BODECKER, C.-D. (1983). *Helv. Chim. Acta*, **66**, 943–959.

GLEITER, R. & SPANGET-LARSEN, J. (1982). *Tetrahedron Lett.* pp. 927–930.

HAGENBUCH, J.-P., VOGEL, P., PINKERTON, A. A. & SCHWARZENBACH, D. (1981). *Helv. Chim. Acta*, **64**, 1818–1832.

HOUK, K. N. (1983). *Theoretical Studies of Alkene Pyramidalizations and Addition Stereoselectivities.* In *Stereochemistry and Reactivity of π-Electron Systems*, edited by W. H. WATSON, pp. 1–40. Florida: Verlag Chemie International.

HOUK, K. N., RONDAN, N. G., BROWN, F. K., JORGENSEN, W. L., MADURA, J. D. & SPELLMEYER, D. C. (1983). *J. Am. Chem. Soc.* **105**, 5980–5988.

JOHNSON, C. K. (1971). *ORTEPII.* Report ORNL-3794. revised. Oak Ridge National Laboratory, Tennessee.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

PAQUETTE, L. A., CARR, R. V. C., CHARUMILIND, P. & BLOUNT, J. P. (1980). *J. Org. Chem.* **45**, 4922–4926.

PINKERTON, A., SCHWARZENBACH, D., STIBBARD, J. H. A., CARRUPT, P.-A. & VOGEL, P. (1981). *J. Am. Chem. Soc.* **103**, 2095–2096.

SPANGET-LARSEN, J. & GLEITER, R. (1983). *Tetrahedron*, **39**, 3345–3350.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUGIMOTO, T., KOBUKE, Y. & FURUKAWA, J. (1976). *J. Org. Chem.* **41**, 1457–1459.

WATSON, W. H., GALLOY, J., BARTLETT, P. D. & ROOF, A. A. M. (1981). *J. Am. Chem. Soc.* **103**, 2022–2031.

WATSON, W. H., GALLOY, J., GROSSIE, D. A., BARTLETT, P. D. & COMBS, G. L. JR (1984). *Acta Cryst.* C40, 1050–1054.

WATSON, W. H., KASHYAP, R. P., BARTLETT, P. D. & WU, C. (1984). *Acta Cryst.* C40, 863–866.

Dimethyl *rel*-(1*R*,4*S*,4a*R*)-2,3,4,4a-Tetrahydro-1,4-methano-1*H*-benzocycloheptene-5,6-dicarboxylate, C₁₆H₁₈O₄

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Abstract. $M_r = 274·32$, monoclinic, $P2_1/c$, $a = 7·659$ (1), $b = 10·833$ (3), $c = 16·867$ (5) Å, $\beta = 96·04$ (2)°, $V = 1391·7$ (6) Å³, $Z = 4$, $D_x = 1·309$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1·54178$ Å, $\mu = 7·77$ cm⁻¹, $F(000) = 584$, room temperature, $R = 0·044$ for 1566 unique reflections with $I > 3\sigma(I)$. The cycloheptatriene ring is in a distorted boat conformation. The two CCOOCH₃ moieties are planar, exhibit extended conformations, and make an interplanar angle of 94·3 (7)°. The norbornane system is slightly twisted because of fusion to the seven-membered ring.

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Introduction. The cycloadditions of dimethyl acetylene-dicarboxylate (DMAD) to the three isomers of isodicyclopentadiene, (1) to (3), have been studied (Paquette & Carr, 1980; Subramanyam, Bartlett, Iglesia, Watson & Galloy, 1982; Bartlett & Wu, 1984). The diene (3) isomer reacts slowly with DMAD at 253 K to give only one product, (4), in good yield. Unlike the cycloadducts of DMAD with isomers (1) and (2), compound (4) is thermally labile due to its *trans*-fused bicyclic nature. When heated in solution to temperatures above 373 K, compound (4) quantitatively undergoes a norbornadiene–cycloheptatriene-type rearrangement (Herndon & Lowry, 1964; Lustgarten &