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The synthesis of the highly strained helical 4-*tert*-butyl-1,5,8-trimethylphenanthrene **6** was achieved by photochemically induced dehydrocyclization. The helical deformation of the aromatic carbon skeleton in the reported X-ray structure is found to be 36.6° which is the largest value found for a phenanthrene hydrocarbon. A systematic quantum chemical investigation of strained 4,5-substituted phenanthrene derivatives (R, R': F, Cl, methyl, *tert*-butyl) at *ab initio* Hartree–Fock and semiempirical AM1 theoretical levels is presented. The geometrical parameters describing the strain in these helical molecules are compared with X-ray data from the literature and are found to be generally in good agreement. Substantial deviations between theory and experiment for the helical deformation angles are observed in the case of the chlorine-substituted molecules (*ca.* 5°) which indicates the importance of crystal packing effects. A prediction of the structure of the unknown 4,5-di-*tert*-butylphenanthrene **5**, that could be detected by GC–MS, but has not been isolable so far is also given. The total strain energies of **5** and **6** are calculated to be 49.6 and 34.0 kcal mol⁻¹, respectively, and are distributed to non-bonded and aromatic ring deformation contributions.

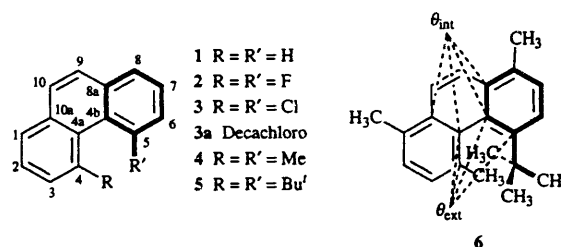
Introduction

There has been continued interest in relationships between structure and physical and chemical properties of strained or sterically hindered aromatic hydrocarbons.^{1–3} Interesting examples of such molecules are phenanthrenes where substitution of large molecular groups in the 4 and 5 positions can lead to a close proximity of the substituents ('overcrowding') which results in a helical distortion of the planar aromatic system.^{4,5} 4,5-Dimethylphenanthrene, which was synthesized in 1940 by Newman,⁶ has been investigated in detail experimentally (UV, CD and X-ray⁷) and theoretically by molecular orbital (MO)^{8,9} and force-field calculations.^{7,10}

Since X-ray data of the 4,5-difluorine and 4,5-dichlorine substituted phenanthrenes are available in the literature¹¹ it seems interesting to increase the substituents further and to look for the changes in chemical and physical properties of the substances. Similar to [n]paracyclophanes, where shortening of the (CH₂)_n chain results in systematically more strained molecules,¹² larger substituents should yield more strained and helical distorted phenanthrenes. To minimize electronic substituent effects hydrocarbon substituents like methyl or *tert*-butyl should be preferred.

In this paper we present the first synthesis and X-ray structure of the highly strained 4-*tert*-butyl-1,5,8-trimethylphenanthrene **6**. Furthermore, a detailed investigation of its structure and strain energy with modern quantum chemical MO methods (*ab initio* HF-SCF and semiempirical AM1¹³) is given. Previous theoretical work with similar methods on [n]helicenes,¹⁴ which are the larger homologues of helical distorted phenanthrenes, has given a detailed understanding of structure–property relationships for large polycyclic aromatic hydrocarbons. These theoretical approaches are used here to elucidate the structures of 4,5-disubstituted phenanthrenes (**1–5**) with various groups of increasing size. The data are discussed in comparison with the corresponding X-ray data taken from the literature.

Compound **6** was prepared by the well known photochemically induced dehydrocyclization reaction^{15–17} from the



Schematic structures of the investigated helical phenanthrenes **1–6**. Compound **6b** lacks the 1- and 8-methyl substituents.

corresponding stilbene precursor using I₂/O₂ as a dehydrogenation agent in 13% yield. As a byproduct 1,4-dimethyl-7-*tert*-butylphenanthrene was isolated. The formation of this compound can be rationalized with the loss of a methyl group during the cyclization step which seems to reduce the large strain energy at this stage of the reaction.

Outline of the calculations

All calculations have been carried out in the framework of Hartree–Fock self-consistent-field (HF-SCF) theory either in an *ab initio* manner or semiempirically using the NDDO integral approximation¹⁸ with the AM1 Hamiltonian.¹³ The *ab initio* orbitals are expanded in a Gaussian AO basis set of valence double- ζ (VDZ) quality (C, F: 7s4p \rightarrow [3s2p]; Cl: 10s7p \rightarrow [4s3p]; H: 4s \rightarrow [2s]).¹⁹ This basis set has given good results for the geometries of larger [n]helicenes¹⁴ at a moderate computational effort. The VDZ basis was augmented with polarization d-functions ($a_d = 0.55$) in the case of the chlorine atom since too long C–Cl bonds (VDZ: 1.87 Å, VDZ + d: 1.82 Å, exp.: 1.83–1.84¹¹) are obtained with the VDZ basis only. Neglecting d-functions on the carbon and fluorine atoms has the effect of bond elongation so that the error in near HF-SCF bond lengths (they are too short due to neglecting the electron correlation effects) is partially compensated. All molecules have been completely optimized in C₂ (C₁ for **6**)

Table 1 Comparison of X-ray and theoretically calculated geometrical parameters of the investigated phenanthrenes

Compound	R, R'	Method ^a	$\theta_{\text{ext}}/^\circ$ ^b	$\theta_{\text{int}}/^\circ$ ^c	$r(\text{C4-C5})/\text{\AA}$	$r(\text{C4a-C4b})/\text{\AA}$	Ref.
1	H, H	X-Ray	2.6	1.5	2.997	1.465	11
		<i>ab initio</i>	0.0	0.0	3.002	1.466	
		AM1	0.0	0.0	2.963	1.446	
2	F, F	X-Ray	20.1	12.7	3.150	—	11
		<i>ab initio</i>	21.8	14.5	3.153	1.469	
		AM1	13.4	10.2	3.087	1.449	
3	Cl, Cl	X-Ray	37.7	24.1	3.211	—	11
		<i>ab initio</i>	33.0	23.2	3.215	1.472	
		AM1	32.0	24.5	3.161	1.449	
3a	Deca Cl Cl, Cl	X-Ray	41.9	27.9	—	1.480	23
		<i>ab initio</i>	41.5	33.0	3.091	1.466	
		AM1	40.5	33.7	3.072	1.448	
4	Me, Me	X-Ray	33.0	22.2	3.271	—	11 7
		X-Ray	31.5	22.7	3.159	1.461	
		<i>ab initio</i>	33.1	22.9	3.190	1.481	
5	Bu ^t , Bu ^t	AM1	31.1	23.8	3.136	1.452	
		<i>ab initio</i>	45.7	35.8	3.345	1.490	
		AM1	45.9	36.7	3.298	1.457	
6 6b	Bu ^t , Me	X-Ray ^d	36.6	28.7	3.165	1.463	
		<i>ab initio</i>	37.9	28.6	3.244	1.484	
		AM1	38.1	30.2	3.203	1.454	

^a Total HF-SCF energies of the molecules are -535.3960 , -732.8678 , -1452.8919 , -5122.9168 , -613.3413 , -847.1951 and -730.2692 au. The AM1 ΔH_f^{298} values are 57.44, -24.36 , 58.45, 35.69, 56.25, 55.92 and 55.92 kcal mol⁻¹. ^b Dihedral angle C4-C4a-C4b-C5 (see Scheme 1). ^c Dihedral angle C8a-C4b-C4a-C10a (see Scheme 1). ^d Average values from two independent structure measurements.

symmetry with the TURBOMOLE (*ab initio*)²⁰ or MOPAC 6.0²¹ (AM1) program systems, respectively.

Results and discussion

Structures

A comparison of X-ray and theoretically calculated geometrical parameters describing the deformation and strain of the investigated phenanthrenes is given in Table 1. Other geometrical parameters not reported here compare very well with each other (the deviations of theoretical bond lengths and bond angles from X-ray data are generally <0.02 Å and $<2^\circ$; respectively). The dihedral angles θ_{ext} and θ_{int} measure the extent of helical twisting of the two outer benzene moieties of the phenanthrene structure towards each other. In most cases θ_{ext} is larger than θ_{int} by *ca.* 50%. Furthermore, the steric overcrowding in the 'bay area' of the molecules reveals itself by elongation of the bonded C4a-C4b and the non-bonded C4-C5 distances. Both r values, θ_{ext} and θ_{int} increase monotonically with increasing size of the substituent independent of the source of the structural data. We begin our discussion with the parent compound phenanthrene which is found to be non-planar in an X-ray analysis.¹¹ The small deformation angles of 2.6 and 1.5°, however, may be caused by crystal packing effects since reliable theoretical methods always found the planar C_{2v} structure as a true minimum. The smallest substituent in our series is the fluorine atom which causes a strong deformation of *ca.* 20° when substituted in the 4 and 5 positions. Here, X-ray and *ab initio* data are in good agreement (deviations in $\theta < 2^\circ$, in $r < 0.005$ Å) while the AM1 value for $\theta_{\text{ext}} = 13.4$ is too small by *ca.* 8°. It should be mentioned here that the deformation in 4,5-substituted phenanthrenes can be rationalized from two competitive effects: planarization which increases stabilizing π -orbital interactions and repulsive non-bonding interactions between the substituents. In the AM1 method, empirical core-core repulsion functions are employed which have been found not always to work correctly for small distances (especially for hydrogen bonds²²). The AM1 F-F repulsion function may be too flat which then results in smaller deformation angles but we cannot exclude that the effect comes from an underestimation of charge repulsion due to the NDDO integral approximation.

For the large chlorine substituents, which increase θ_{ext} again

(by *ca.* 13°), the situation is different. Here, X-ray and AM1/*ab initio* data disagree by *ca.* 5° for θ_{ext} while θ_{int} and the r values compare very well with each other. To get more insight into these discrepancies we have investigated the computationally very expensive decachlorine-substituted compound **3a** for which X-ray data are also available.²³ In this case all θ_{ext} values are within 1° but the experimental θ_{int} value is now lower by *ca.* 5°. Because the X-ray data may suffer from crystal packing and disordering effects or from problems with the numerical analysis of the diffraction data, a comparison of the two X-ray parameter sets of **4** taken from the literature allow a reliable estimation of the 'normal' experimental accuracy, *i.e.* 2° for θ , 0.1 Å for non-bonded and 0.02 Å for bonded atom-atom distances. With the exception of **3** and **3a** discussed above, AM1 and *ab initio* data are in any case within these error limits (for **1** bond lengths from X-ray and *ab initio* structures agree with one exception to within 0.01 Å). However, the AM1 geometries are slightly different in that the r values are generally too short and the θ_{int} are too large. Thus, because the theoretical methods employed (especially the *ab initio* ones) are in general very reliable for the prediction of nuclear geometries, there are two possible explanations for the discrepancies in the case of the chlorine-substituted molecules: First, the errors of the experimental structure determinations may lead to incorrect θ values. Secondly, crystal packing effects (for a general discussion see ref. 24) due to larger intermolecular forces may be quite important in the case of the more polarizable chlorine substituents and these flat potential energy surfaces for the twisting motion. This idea is supported by the shortest intermolecular chlorine-chlorine distances of 3.56 and 3.36 Å, respectively, found in the crystal structures of **3** and **3a**.^{11,23} It should also be mentioned here that we cannot exclude errors of the HF-SCF treatment with an incomplete basis set and some effects from the neglect of electron correlation. However, it seems unusual that such errors should manifest themselves only in one geometric variable. Furthermore, we have used two quite different theoretical approaches which give θ values within 1° for **3** and **3a**.†

† A density-functional calculation of **3** with the B3-LYP functional (which includes to some extent electron correlation effects) and a VDZP AO-basis gives $\theta_{\text{ext}} = 33.4$ and $\theta_{\text{int}} = 22.7^\circ$ in very good agreement with the HF-SCF values ($\theta_{\text{ext}} = 33.0$ and $\theta_{\text{int}} = 23.2^\circ$).

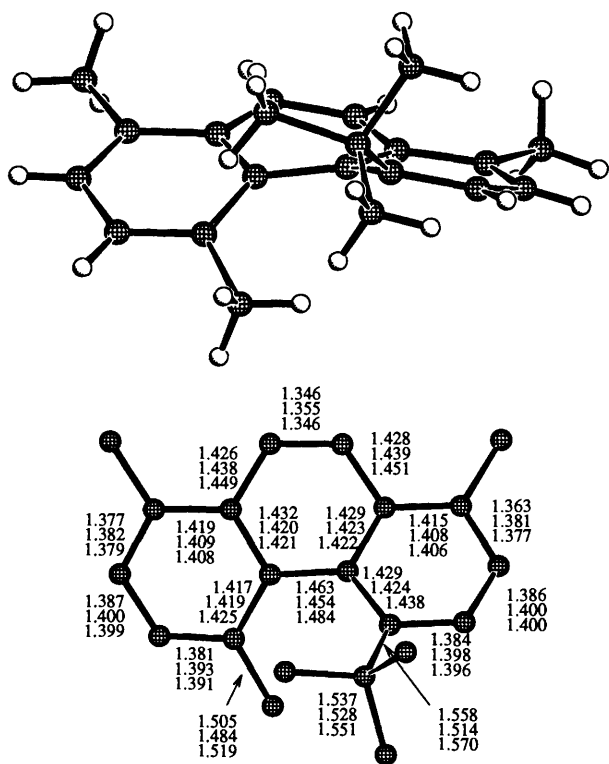


Fig. 1 Crystal structure of the 4-*tert*-butyl-5-methyl substituted phenanthrene **6**. The top number is the bond length obtained from the X-ray analysis (average values from two independent structure measurements), the middle and bottom values refer to AM1 and *ab initio* HF-SCF calculations of **6b**, respectively. The three C-C bond lengths in the *tert*-butyl group have been averaged.

For the 4,5-dimethyl- and the 4,5-methyl-*tert*-butyl-substituted phenanthrenes all geometries investigated are in good agreement. For the latter compound we compare the experimentally investigated trimethyl-*tert*-butyl substituted molecule **6** with the computationally simpler parent 4-*tert*-butyl-5-methylphenanthrene (**6b**). The X-ray structure and a comparison of experimental and theoretical bond lengths are shown in Fig. 1. The unit cell of the crystal of **6** contains four molecules and shows no special features. There are two independent but nearly identical molecules forming an asymmetric unit in the cell. With the exception of the C(sp²)-C(sp³) and the C-C bonds in the *tert*-butyl group, which are too short at the AM1 level, all values are within a range of 0.02 Å (<0.01 Å in most cases). Inspection of Fig. 1 demonstrates not only the helical deformation but a significant boat-type deformation of the outer benzene rings also, which is similar to the case of [*n*]paracyclophanes.³

If we neglect the X-ray data of **3**, where the deviations between theory and experiment are not yet fully resolved, the synthesized *tert*-butyl-methyl compound **6** shows to our knowledge the largest reported deformation angles $\theta_{\text{ext}} = 36.6^\circ$ and $\theta_{\text{int}} = 28.7^\circ$ of a 4,5-disubstituted phenanthrene. Larger values are found theoretically only for the di-*tert*-butyl structure ($\theta_{\text{ext}} = 46^\circ$ and $\theta_{\text{int}} = 36^\circ$). Unfortunately, the photochemically induced dehydrocyclization synthesis starting from 1,2-bis(5-*tert*-butyl-2-methylphenyl)ethene gave only a very low concentration of the 4,5-di-*tert*-butyl-1,8-dimethylphenanthrene in the reaction mixture (GC-MS analysis has indicated its presence) from which isolation failed.

Strain energies

For the 4-*tert*-butyl-5-methylphenanthrene we have calculated the total strain energy (SE) and its various contributions at the *ab initio* HF-SCF level. *tert*-Butyl and methyl substituents were

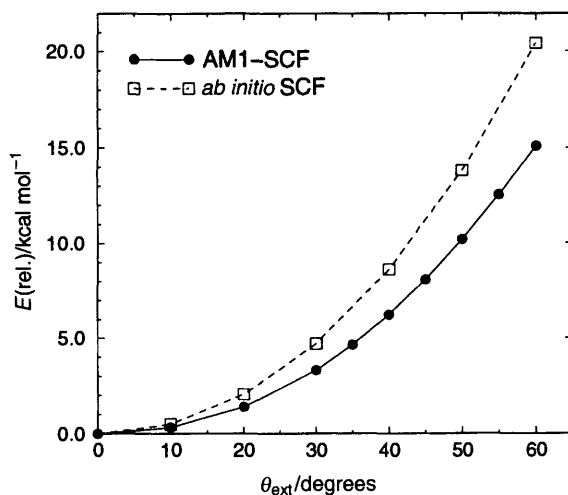


Fig. 2 Dependence of the relative energy of phenanthrene **1** on the deformation angle θ_{ext} at *ab initio* HF-SCF and AM1 theoretical levels. The data correspond to fully AM1 optimized structures (except θ_{ext} which is the reaction coordinate) which were employed in single-point HF-SCF calculations.

replaced by hydrogen atoms pointing in the original direction [$r(\text{CH}) = 1.08 \text{ \AA}$] but retaining the rest of the optimized nuclear geometry of **6b**. The energy difference with respect to an optimized phenanthrene structure then yields a strain energy of $25.5 \text{ kcal mol}^{-1}$ ($1 \text{ cal} = 4.184 \text{ J}$) for the aromatic skeleton deformation. Application of a similar procedure to the two substituents yields the sum of interaction and internal substituent strain energies ($8.5 \text{ kcal mol}^{-1}$). By increasing the distance of the methane and isobutane molecules with respect to each other to 15 \AA but retaining their original geometries we have obtained values of 3.9 and $4.6 \text{ kcal mol}^{-1}$ for the repulsive interaction and internal substituent strain energy, respectively. These data show clearly that the dominating destabilizing factor in **6b** is the aromatic ring deformation.

To get more insight into the ring contributions to the strain energy in phenanthrenes, potential energy curves for the helical deformation of phenanthrene (model compound) with θ_{ext} as the reaction coordinate have been calculated. The data shown in Fig. 2 correspond to fully optimized AM1 structures which were then employed in single-point HF-SCF calculations. Both calculational approaches show similar quadratic potentials for the ring deformation but with a tendency of the AM1 function to be too flat. This result is consistent with the observed underestimation of AM1 rotational barriers in conjugated systems.²⁵

Small relative energies below 5 kcal mol^{-1} are found for $\theta_{\text{ext}} < 30^\circ$ which indicates that the phenanthrene structure does not have a very rigid carbon skeleton. Deformation angles below 5° have a negligible energetic effect which explains the non-planar phenanthrene structure found in non-homogeneous environments.¹¹ The energy increase at $\theta_{\text{ext}} = 38^\circ$ (value of **6**) is lower by a factor of three than the ring strain energy calculated above. This can be attributed to the fact that the deformation induced by the substituents is not only measured by the θ angles alone but is distributed to the whole aromatic system. Thus, phenanthrene with a frozen dihedral angle θ_{ext} is only a crude model for the distribution of strain in substituted compounds.

The total SE of **5** is calculated to be $49.6 \text{ kcal mol}^{-1}$, *i.e.* $15.6 \text{ kcal mol}^{-1}$ larger than for **6b**† with an aromatic ring SE of $38.3 \text{ kcal mol}^{-1}$, an internal substituent contribution of $7.6 \text{ kcal mol}^{-1}$ and non-bonded substituent interactions of 3.7 kcal

† Using unstrained total energy increments (HF-SCF/SV) for CH₃, CH and C groups, SE values of 41.3 and $63.1 \text{ kcal mol}^{-1}$ are obtained for **6b** and **5**, respectively.

mol⁻¹. Similar to the case of **6**, SE(arom.) is three times larger than the value derived from the potential energy curve of **1** at $\theta_{\text{ext}} = 46^\circ$.

Conclusions

The steric interactions of substituents in 4- and 5-positions result in non-planar helical phenanthrene structures. Experimental X-ray and theoretical structures show that the helical deformation increases with increasing size of the substituents. Electronic effects are indicated by comparison of **3** (R = R' = Cl) and the decachlorine compound **3a**, i.e. a large number of electron-withdrawing groups destabilizes the π -system which results in a larger helical deformation. The good performance of the *ab initio* HF-SCF method for the prediction of the nuclear geometries allows us to assess some discrepancies between theory and experiment to significant crystal packing effects in the case of the chlorine substituted molecules.

The 4-*tert*-butyl-1,5,8-trimethylphenanthrene molecule, which was prepared and structurally characterized for the first time, is the most highly overcrowded disubstituted phenanthrene system. The total strain energy per carbon atom (1.8 kcal mol⁻¹) is between the values of [6]- and [7]-paracyclophane (2.7 and 1.2 kcal mol⁻¹ respectively, AM1 data¹²). The theoretical methods predict an increase of ca. 10° for the deformation angles θ when replacing the 5-methyl group by a second *tert*-butyl substituent. Due to the quadratic nature of the aromatic ring deformation potential the di-*tert*-butylphenanthrene molecule is highly strained (SE_{tot} = 49.6, 2.3 kcal mol⁻¹ per carbon atom) so that it represents an interesting challenge for organic synthesis.

Experimental

4-*tert*-Butyl-1,5,8-trimethylphenanthrene **6**

A stirred solution of 278 mg (1 mmol) of 1-(5-*tert*-butyl-2-methylphenyl)-2-(2,5-dimethylphenyl)ethene and 254 mg (1 mmol) of iodine in 400 ml of cyclohexane was irradiated for 8 h with unfiltered UV-light (high-pressure mercury lamp, TQ 150 Heraeus, 150 W). The course of the reaction was monitored by GC-MS-analysis of iodine-free samples. After irradiation the mixture was shaken with saturated sodium thiosulfate solution (150 ml) and water. The organic layer was dried over Na₂SO₄, the solvent was evaporated and the residue was purified by chromatography (SiO₂; R_f = 0.35 (light petrol, 40–60 °C) to yield 36.4 mg (13%) of colourless crystals: mp 83 °C (ethanol-water); δ_{H} (250 MHz, CDCl₃; *J* values in Hz) 1.17 (s, 9 H, Bu'), 2.55 (s, 3 H, CH₃), 2.65 (s, 3 H, CH₃), 2.70 (s, 3 H, CH₃), 7.03 (d, ³*J*_{HH} 7.3, 1 H, HAr), 7.24 (d, ³*J*_{HH} 7.3, 1 H, HAr), 7.30 (d, ³*J*_{HH} 7.7, 1 H, HAr), 7.58 (d, ³*J*_{HH} 7.7, 1 H, HAr), 7.63 (d, ³*J*_{HH} 9.1, 1 H, HAr), 7.70 (d, ³*J*_{HH} 9.1, 1 H, HAr); δ_{C} (62.9 MHz, CDCl₃) 19.00 (1 CH₃), 19.45 (1 CH₃), 22.78 (1 CH₃), 33.38 (3 CH₃, Bu'), 39.63 [1 Cq (quaternary C), Bu'], 121.65 (2 CH), 125.28 (1 CH), 126.05 (1 CH), 126.79 (1 CH), 127.06 (1 CH), 127.59 (1 Cq), 129.40 (1 Cq), 130.18 (1 Cq), 131.66 (1 Cq), 132.14 (1 Cq), 132.29 (1 Cq), 135.34 (1 Cq), 147.13 (1 Cq, C-Bu'); GC-MS *m/z* 276 (M⁺ [C₂₁H₂₄], 56%), 261 (M⁺ - CH₃, 20%), 246 (M⁺ - 2 CH₃, 18%), 219 (M⁺ - C₄H₉, 100 (219 - CH₃, 34%), 189 (219 - 2 CH₃, 17%), (C₄H₉, 14%); C₂₁H₂₄ (276.42); calc. C, 91.25; H, 8.75, found C, 91.15; H, 8.63.

X-Ray structure of (±)-4-*tert*-butyl-1,5,8-trimethylphenanthrene (**6**)

Crystal data: C₂₁H₂₄, M_w 276.4 g mol⁻¹, colourless crystals, dimensions 0.65 × 0.50 × 0.25 mm, D_c 1.13 g cm⁻³, triclinic, space group P $\bar{1}$ (No. 2), *a* = 11.245(2), *b* = 11.422(3), *c* = 13.873(3) Å, α = 69.36(2), β = 83.28(2), γ = 77.67(2)°, *V* = 1627.3(6) Å³, Z = 4, F(000) = 600. A total of 7645 reflections

were recorded on a Nicolet R3m diffractometer (graphite monochromator, λ (Mo-K α) = 0.710 73 Å, μ (Mo-K α) = 0.063 mm⁻¹), at T = 293(2) K. Of these, 4260 independent reflections were used the structure solution (SHELXTL-PLUS²⁶) and refinement (391 parameters, SHELXL-93²⁷). Non-hydrogen atoms were refined anisotropically (full-matrix least-squares refinement on F²); H atoms were refined using a riding model, $wR_2 = 0.115$ [*R* for *F* > 4 σ (*F*) = 0.042]. Largest difference peak 0.130 e Å⁻³.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/32.

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References

- 1 L. Salem, *The Molecular Orbital Theory of Conjugated Systems*, Benjamin, Reading, 1966.
- 2 H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules*, Academic Press, New York, 1967.
- 3 A. Greenberg and J. F. Liebman, *Strained Organic Molecules*, Academic Press, New York, 1978.
- 4 H. Scherübl, U. Fritsche and A. Mannschreck, *Chem. Ber.*, 1984, **117**, 336.
- 5 R. Fritsch, E. Hartmann, G. Brandl and A. Mannschreck, *Tetrahedron: Asymmetry*, 1993, **3**, 433.
- 6 M. S. Newman, *J. Am. Chem. Soc.*, 1940, **62**, 2295.
- 7 R. N. Armstrong, H. L. Ammon and J. N. Darnow, *J. Am. Chem. Soc.*, 1987, **109**, 2077.
- 8 V. Buss and K. Kolster, *Z. Phys. Chem. N.F.*, 1989, **162**, 73.
- 9 S. Grimme and H.-G. Löhmannsröben, *J. Phys. Chem.*, 1992, **96**, 7005.
- 10 J. Kao and N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 975.
- 11 R. Cosmo, T. W. Hambley and S. Sternhell, *J. Org. Chem.*, 1987, **52**, 3119.
- 12 F. Bockisch, J. C. Rayez, D. Liotard and B. Duguay, *J. Comp. Chem.*, 1992, **13**, 1047.
- 13 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
- 14 S. Grimme and S. D. Peyerimhoff, *Chem. Phys.*, 1996, **204**, 411.
- 15 W. H. Laarhoven, *Recl. Trav. Pays-Bays*, 1983, **102**, 185.
- 16 C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.
- 17 F. B. Mallory and C. B. Mallory, *Org. React.*, 1984, **30**, 1.
- 18 J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, 129.
- 19 A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571.
- 20 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165.
- 21 J. J. P. Stewart, *QCPE Bull.*, 1985, **5**, 133.
- 22 W. Thiel, *Tetrahedron*, 1988, **44**, 7393.
- 23 F. H. Herbstein, M. Kapon and R. Merksamer, *Acta Crystallogr., Sect. B*, 1976, **32**, 2205.
- 24 A. Gavezzatti, 'Molecular Packing and Correlations between Molecular and Crystal Properties' in *Structure Correlation*, eds. H.-B. Bürgi and J. D. Dunits, VCH, Weinheim 1994, pp. 509–542.
- 25 W. M. F. Fabian, *J. Comp. Chem.*, 1988, **9**, 369.
- 26 G. M. Sheldrick, *SHELXTL-Plus*, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1989.
- 27 G. M. Sheldrick, *SHELXL-93*, Universität Göttingen, 1993.

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