

## Dibenzo[def,pqr]tetraphenylene (Bi-4,5-phenanthrylene)

BY H. IRNGARTINGER AND W. R. K. REIBEL

*Institut für Organische Chemie der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg,  
Federal Republic of Germany*

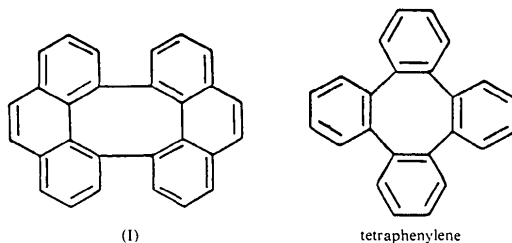
AND GEORGE M. SHELDRICK†

*Anorganisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen,  
Federal Republic of Germany*

(Received 6 December 1980; accepted 20 January 1981)

**Abstract.**  $C_{28}H_{16}$ ,  $M_r = 352.44$ , monoclinic,  $Cc$ ,  $a = 30.492(4)$ ,  $b = 7.405(4)$ ,  $c = 16.362(4)$  Å,  $\beta = 105.30(1)^\circ$ ,  $U = 3563.5$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.314$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.069$  mm<sup>-1</sup>. The structure was solved by incorporating trio relations into the starting set for multiresolution direct methods, and refined to  $R = 0.048$  for 3947 unique observed reflexions. The molecule shows a distorted tub conformation. The phenanthrene moieties are twisted considerably. The racemate consists of helical PP and MM enantiomers.

**Introduction.** Cyclooctatetraene and its derivatives show non-planar tub conformations (Fray & Saxton, 1978). Tetraphenylene, a tetrabenzocyclooctatetraene, has the same geometry (Irngartinger & Reibel, 1981). Some bridged tetraphenylene derivatives have been synthesized and non-planar conformations postulated from spectroscopic data (Hellwinkel & Haas, 1979; Hellwinkel, Reiff & Nykodym, 1977). We determined the structure of dibenzo[def,pqr]tetraphenylene (I), a bi-4,5-phenanthrylene (Thulin & Wennerström, 1977), to establish the molecular conformation.



Recrystallization of (I) from cyclohexane afforded colourless prisms. The cell dimensions were derived by least squares from 47 high-order reflexions ( $2\theta \geq 42^\circ$ ) measured with Mo  $K\alpha$  radiation on a diffractometer. A crystal  $0.62 \times 0.51 \times 0.24$  mm was mounted along  $b^*$  on a computer-controlled diffractometer (Siemens

AED). 4418 reflexions were recorded for  $\sin \theta/\lambda \leq 0.664$  Å<sup>-1</sup> with graphite-monochromated Mo  $K\alpha$  radiation. After application of Lp corrections, averaging equivalents gave 4328 unique reflexions, of which 3947 with  $F > 4\sigma(F)$  were employed for structure refinement. The noncentrosymmetric space group  $Cc$  derived from the  $N(Z)$  test (Howells, Phillips & Rogers, 1950) and  $E$  statistics was confirmed by refinement. Therefore there are two independent molecules in the asymmetric unit. Attempts to solve the structure by direct methods in a routine manner were unsuccessful. The problem was eventually solved by incorporating three trio relations, each consisting of an internally consistent combination of two negative and one positive quartet (Hauptman & Green, 1976; Giacovazzo, 1976), into the starting set for multiresolution direct methods. The solution with the second best value of NQEST (De Titta, Edmonds, Langs & Hauptman, 1975) revealed about half the structure. The remaining atoms were found by Fourier methods. In the final cycles of least-squares refinement, the C atoms were anisotropic and the H atoms were refined freely with individual isotropic temperature factors. Complex neutral-atom scattering-factors and the weighting scheme  $w = [\sigma^2(F) + 0.001F^2]^{-1}$  were employed. The refinement converged to  $R' = \sum w^{1/2}\Delta / \sum w^{1/2}|F_o| = 0.0495$  and  $R = 0.0481$ . Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1, and the molecular geometry in Tables 2–4.\*

**Discussion.** The bond lengths and angles of (I) (Table 2) agree well (within  $3\sigma$ ) with the corresponding values for phenanthrene (Kay, Okaya & Cox, 1971). How-

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35939 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† To whom correspondence should be addressed.

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ )

An asterisk denotes the equivalent isotropic temperature factor calculated as  $\frac{1}{3}$  (trace of the orthogonalized  $U_{ij}$  matrix).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
C(11)	4523 (1)	3948 (3)	387 (1)	386 (7)*
C(12)	4725 (1)	4143 (3)	-291 (1)	410 (7)*
C(13)	4443 (1)	4558 (4)	-1089 (2)	489 (9)*
H(13)	4574 (10)	4686 (40)	-1509 (21)	543 (72)
C(14)	3974 (1)	4713 (4)	-1226 (2)	580 (10)*
H(14)	3807 (12)	5056 (49)	-1740 (23)	734 (84)
C(15)	3775 (1)	4270 (4)	-601 (2)	577 (10)*
H(15)	3456 (9)	4184 (32)	-675 (16)	374 (59)
C(16)	4044 (1)	3814 (3)	206 (2)	487 (9)*
C(17)	3846 (1)	3103 (4)	84 (2)	582 (10)*
H(17)	3514 (10)	3105 (37)	681 (17)	465 (65)
C(21)	4785 (1)	3746 (3)	1257 (1)	393 (7)*
C(22)	5209 (1)	4612 (3)	1582 (1)	381 (7)*
C(23)	5456 (1)	4198 (4)	2405 (1)	440 (8)*
H(23)	5730 (9)	4770 (36)	2598 (16)	429 (63)
C(24)	5290 (1)	3011 (4)	2915 (2)	500 (9)*
H(24)	5502 (10)	2702 (37)	3480 (18)	492 (68)
C(25)	4855 (1)	2384 (4)	2642 (2)	511 (10)*
H(25)	4730 (10)	1534 (39)	3043 (18)	489 (67)
C(26)	4587 (1)	2801 (3)	1826 (2)	454 (8)*
C(27)	4106 (1)	2489 (4)	1581 (2)	545 (10)*
H(27)	3986 (10)	1866 (38)	2025 (18)	483 (66)
C(31)	5588 (1)	4729 (4)	5 (1)	388 (8)*
C(32)	5203 (1)	3613 (3)	-283 (1)	406 (8)*
C(33)	5240 (1)	2095 (4)	-756 (2)	510 (10)*
H(33)	4989 (11)	1254 (41)	-943 (20)	575 (75)
C(34)	5638 (1)	1682 (5)	-982 (2)	593 (11)*
H(34)	5647 (11)	608 (41)	-1296 (20)	558 (72)
C(35)	5987 (1)	2885 (5)	-803 (2)	605 (12)*
H(35)	6249 (12)	2636 (45)	-989 (22)	794 (86)
C(36)	5965 (1)	4459 (4)	-339 (1)	482 (10)*
C(37)	6280 (1)	5936 (5)	-284 (2)	591 (12)*
H(37)	6509 (12)	5840 (39)	-468 (21)	601 (75)
C(41)	5596 (1)	6251 (3)	557 (1)	371 (7)*
C(42)	5366 (1)	6255 (3)	1209 (1)	390 (8)*
C(43)	5356 (1)	7846 (4)	1644 (2)	493 (9)*
H(43)	5204 (11)	7842 (43)	2051 (20)	647 (76)
C(44)	5574 (1)	9408 (4)	1492 (2)	560 (10)*
H(44)	5558 (9)	10487 (41)	1758 (18)	432 (64)
C(45)	5848 (1)	9347 (4)	947 (2)	554 (10)*
H(45)	6007 (12)	10541 (47)	854 (21)	698 (82)
C(46)	5876 (1)	7757 (4)	499 (1)	457 (9)*
C(47)	6216 (1)	7528 (5)	46 (2)	553 (10)*
H(47)	6402 (12)	8619 (39)	2 (20)	588 (73)
C(51)	3414 (1)	-1013 (3)	-160 (1)	412 (8)*
C(52)	3215 (1)	-805 (3)	-1042 (1)	408 (8)*
C(53)	3499 (1)	-396 (4)	-1558 (2)	488 (9)*
H(53)	3358 (11)	-156 (43)	-2163 (22)	623 (76)
C(54)	3969 (1)	-250 (4)	-1226 (2)	573 (11)*
H(54)	4152 (12)	105 (46)	-1590 (21)	691 (80)
C(55)	4166 (1)	-721 (4)	-404 (2)	595 (11)*
H(55)	4518 (9)	-841 (33)	-176 (17)	413 (61)
C(56)	3891 (1)	-1180 (3)	134 (2)	496 (9)*
C(57)	4084 (1)	-1908 (4)	969 (2)	593 (10)*
H(57)	4406 (9)	-2079 (33)	1128 (15)	359 (58)
C(61)	3147 (1)	-1207 (3)	443 (1)	409 (7)*
C(62)	2723 (1)	-346 (3)	342 (1)	390 (7)*
C(63)	2470 (1)	-760 (4)	911 (1)	450 (8)*
H(63)	2172 (8)	-262 (35)	831 (15)	392 (61)
C(64)	2629 (1)	-1955 (4)	1580 (2)	524 (10)*
H(64)	2437 (10)	-2218 (39)	1941 (19)	524 (70)
C(65)	3062 (1)	-2583 (4)	1744 (2)	541 (10)*

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(65)	3203 (8)	-3244 (35)	2267 (16)	356 (57)
C(66)	3336 (1)	-2163 (3)	1201 (1)	465 (8)*
C(67)	3819 (1)	-2496 (4)	1438 (2)	570 (10)*
H(67)	3926 (11)	-3260 (41)	1930 (21)	570 (73)
C(71)	2354 (1)	-240 (4)	-1603 (1)	408 (8)*
C(72)	2740 (1)	-1350 (3)	-1507 (1)	408 (8)*
C(73)	2710 (1)	-2885 (4)	-2009 (2)	540 (10)*
H(73)	2986 (12)	-3695 (40)	-1953 (20)	588 (74)
C(74)	2314 (1)	-3313 (5)	-2619 (2)	649 (12)*
H(74)	2310 (10)	-4414 (39)	-2914 (18)	456 (66)
C(75)	1957 (1)	-2136 (5)	-2786 (2)	677 (12)*
H(75)	1691 (12)	-2174 (43)	-3233 (22)	726 (81)
C(76)	1974 (1)	-542 (4)	-2316 (1)	520 (10)*
C(77)	1653 (1)	894 (5)	-2577 (2)	639 (12)*
H(77)	1394 (15)	561 (52)	-3133 (26)	990 (98)
C(81)	2340 (1)	1292 (3)	-1067 (1)	384 (8)*
C(82)	2570 (1)	1312 (3)	-190 (1)	384 (8)*
C(83)	2579 (1)	2913 (4)	257 (2)	483 (9)*
H(83)	2747 (11)	2894 (40)	841 (19)	623 (74)
C(84)	2359 (1)	4465 (4)	-128 (2)	579 (12)*
H(84)	2370 (10)	5524 (41)	166 (19)	461 (65)
C(85)	2086 (1)	4371 (4)	-935 (2)	566 (12)*
H(85)	1912 (11)	5439 (48)	-1174 (21)	671 (80)
C(86)	2054 (1)	2772 (4)	-1405 (2)	482 (10)*
C(87)	1710 (1)	2494 (5)	-2195 (2)	605 (12)*
H(87)	1540 (18)	3620 (58)	-2345 (30)	1181 (108)

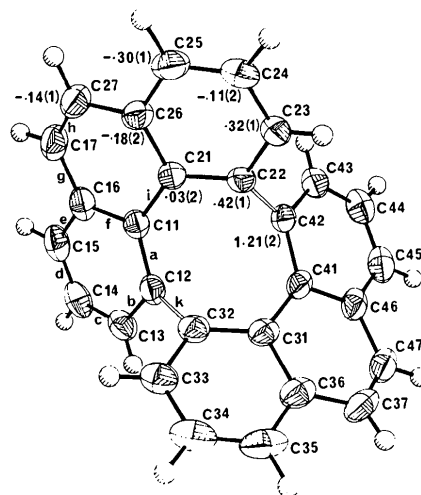


Fig. 1. The first molecule [C(11) to H(47)] with 50% thermal ellipsoids for the C atoms, bond labelling, and mean distances from the phenanthrene plane. The thermal motion of the second molecule is very similar.

ever the phenanthrene subunits of (I) show helical deformations similar to those found in helicenes (Martin, 1974). Both subunits have the same helicity. Because of the glide planes the crystals are racemic mixtures of PP and MM enantiomers. The averaged deviations from the planes of the phenanthrene moieties are given in Fig. 1. The phenyl rings of the biphenyl groups appear to be deformed in a boat-like manner, whereas the connecting phenyl rings of the phenan-

Table 2. Bond lengths (Å)

The bond labelling is shown in Fig. 1.

Ring/Bond	a	b	c	d	e	f	g	h	i	k
1	1.411 (4)	1.393 (3)	1.393 (4)	1.360 (5)	1.401 (4)	1.415 (3)	1.433 (4)	1.339 (4)	1.445 (3)	1.506 (4)
2	1.415 (3)	1.392 (3)	1.396 (4)	1.364 (4)	1.402 (3)	1.421 (4)	1.433 (4)			
3	1.412 (3)	1.386 (4)	1.393 (5)	1.360 (5)	1.404 (5)	1.422 (4)	1.441 (4)	1.332 (5)	1.440 (3)	1.496 (4)
4	1.423 (3)	1.382 (4)	1.388 (4)	1.374 (5)	1.402 (4)	1.422 (4)	1.436 (4)			
5	1.420 (3)	1.392 (4)	1.396 (4)	1.364 (4)	1.410 (5)	1.411 (3)	1.442 (4)	1.324 (5)	1.443 (4)	1.503 (3)
6	1.412 (3)	1.390 (4)	1.392 (4)	1.358 (4)	1.405 (4)	1.413 (3)	1.441 (4)			
7	1.412 (4)	1.392 (4)	1.387 (4)	1.366 (5)	1.402 (5)	1.426 (3)	1.433 (4)	1.329 (5)	1.441 (4)	1.507 (3)
8	1.421 (3)	1.388 (4)	1.395 (4)	1.364 (4)	1.401 (4)	1.419 (4)	1.449 (4)			
Mean	1.416 (5)	1.389 (4)	1.393 (3)	1.364 (5)	1.403 (3)	1.419 (5)	1.439 (6)	1.331 (6)	1.442 (2)	1.503 (5)

Table 3. Bond angles (°)

Ring/Angle	ab	bc	cd	de	ef	af	fi
1	118.1 (2)	121.4 (3)	120.2 (2)	120.0 (3)	119.7 (3)	118.9 (2)	118.0 (2)
2	118.2 (2)	121.8 (2)	119.6 (2)	120.7 (3)	119.3 (2)	118.7 (2)	118.5 (2)
3	118.6 (3)	122.1 (3)	119.2 (3)	120.9 (3)	119.4 (3)	118.3 (2)	118.5 (2)
4	118.1 (2)	122.8 (3)	119.3 (3)	119.9 (3)	120.3 (3)	118.1 (2)	118.9 (2)
5	118.2 (2)	121.3 (3)	120.3 (3)	119.8 (2)	119.7 (2)	118.8 (2)	118.4 (2)
6	118.3 (2)	121.9 (3)	119.4 (3)	120.6 (3)	119.6 (2)	118.5 (2)	118.5 (2)
7	119.2 (2)	121.3 (3)	119.8 (3)	121.0 (3)	119.1 (3)	118.2 (2)	118.3 (2)
8	118.5 (2)	121.7 (2)	119.6 (3)	120.6 (3)	119.6 (2)	118.2 (2)	119.0 (2)
Mean	118.4 (4)	121.8 (5)	119.7 (4)	120.4 (5)	119.6 (4)	118.5 (3)	118.5 (3)

Ring/Angle	gf	eg	gh	bk	ak	ai
1	118.9 (2)	121.3 (3)	121.3 (3)	114.9 (2)	126.0 (2)	123.0 (2)
2	118.4 (2)	121.9 (3)	121.0 (3)	115.1 (2)	125.1 (2)	122.4 (2)
3	117.6 (3)	122.5 (3)	122.0 (3)	115.3 (2)	124.7 (2)	122.8 (2)
4	117.9 (3)	121.4 (3)	121.2 (3)	115.4 (2)	125.4 (2)	122.8 (2)
5	118.7 (3)	121.5 (2)	120.9 (2)	115.1 (2)	125.6 (2)	122.6 (2)
6	118.2 (3)	121.9 (2)	121.6 (3)	115.1 (2)	124.8 (2)	122.7 (2)
7	118.1 (3)	122.5 (2)	121.7 (2)	114.9 (2)	124.4 (2)	123.2 (2)
8	117.6 (3)	122.6 (3)	121.4 (3)	115.5 (2)	124.7 (2)	122.5 (2)
Mean	118.2 (5)	122.0 (5)	121.4 (4)	115.2 (2)	125.1 (5)	122.8 (3)

Table 4. Averaged torsion angles (°)

<i>baf</i>	12.5 (6)	<i>abc</i>	-2.1 (3)
<i>iaa'</i>	20.6 (12)	<i>bcd</i>	-7.0 (7)
<i>aka'</i>	-87.4 (8)	<i>cde</i>	5.3 (8)
<i>aia'</i>	34.6 (11)	<i>def</i>	5.2 (5)
<i>fff'</i>	22.8 (3)	<i>afe</i>	-14.1 (6)
<i>fgg'</i>	-2.3 (8)	<i>gfi</i>	-14.5 (8)
<i>ghg'</i>	11.0 (3)		

threne systems of (I) are twisted (see also torsion angles in Table 4). The marginal deviations from planarity of the unsubstituted phenanthrene are ten times smaller (Kay *et al.*, 1971). The average angle between the planes of the phenyl rings in the biphenyl groups, and the angle between these rings and the connecting phenyl rings, are 26.6 (6) and 15.2 (10)° respectively. The corresponding angles for phenanthrene are 1 to 2°. The angles between the two phenanthrene moieties of the two independent molecules of (I) are 68.4 and 68.7° respectively.

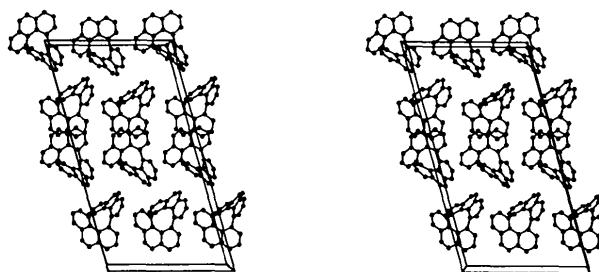


Fig. 2. Stereo packing diagram viewed down *b*. The lack of a twofold axis down the view direction confirms that the space group is *Cc* rather than *C2/c*.

The tub form of the central eight-membered ring is also distorted. The unstrained tetraphenylene has torsion angles of 66.1 and 1.0° (Irrgartinger & Reibel, 1981). The corresponding angles of (I) are 34.6, -87.4 and 20.6° (Table 4). All chemically equivalent dimensions of the two independent molecules of (I) agree well.

Fig. 2 shows the packing in the unit cell.

We thank Professor Hellwinkel and Dr Haas for providing the crystals, and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

#### References

- DE TITTA, G. T., EDMONDS, J. W., LANGS, D. A. & HAUPTMAN, H. (1975). *Acta Cryst.* **A31**, 472–479.  
FRAY, G. I. & SAXTON, R. G. (1978). *The Chemistry of Cyclooctatetraene and its Derivatives*. Cambridge Univ. Press.  
GIACOVAZZO, C. (1976). *Acta Cryst.* **A32**, 74–82.

- HAUPTMAN, H. & GREEN, E. A. (1976). *Acta Cryst.* **A32**, 45–49.  
HELLWINKEL, D. & HAAS, G. (1979). *Justus Liebigs Ann. Chem.* pp. 145–149.  
HELLWINKEL, D., REIFF, G. & NYKODYM, V. (1977). *Justus Liebigs Ann. Chem.* pp. 1013–1025.  
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210–213.  
IRNGARTINGER, H. & REIBEL, W. R. K. (1981). *Acta Cryst.* **B37**, 1724–1728.  
KAY, M. I., OKAYA, Y. & COX, D. E. (1971). *Acta Cryst.* **B27**, 26–33.  
MARTIN, R. H. (1974). *Angew. Chem.* **86**, 727–738.  
THULIN, B. & WENNERSTRÖM, O. (1977). *Tetrahedron Lett.* pp. 929–930.

*Acta Cryst.* (1981). **B37**, 1771–1773

### Structure of 4-Ethynyl-1,2,2,6,6-pentamethyl-4-piperidinol\*

BY M. CYGLER

*Department of Crystallography, Institute of Chemistry, University of Łódź, 91-416 Łódź, Nowotki 18, Poland*

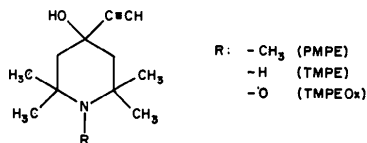
(Received 9 October 1979; accepted 11 March 1981)

**Abstract.**  $C_{12}H_{21}NO$ , monoclinic,  $P2_1/c$ ,  $a = 13.744$  (3),  $b = 7.477$  (2),  $c = 11.477$  (3) Å,  $\beta = 76.68$  (5)°,  $V = 1147.3$  Å<sup>3</sup>,  $D_x = 1.131$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 432$ ,  $\mu(Cu K\alpha) = 0.15$ . The structure was solved by direct methods and refined to  $R = 0.053$  for 1489 independent reflexions with  $I > 3\sigma(I)$ . The molecule exists in a distorted chair conformation with the methyl group equatorial at the N atom and with an equatorial ethynyl group. Two weak intermolecular O—H...N and  $\equiv C-H...O$  hydrogen bonds are formed.

**Introduction.** 2,2,6,6-Tetramethylpiperidine derivatives form simple overcrowded systems with strong steric interactions. Substituents in position 4 lead to additional strain and cause a decrease of the energy barrier between chair and twist or boat conformations of the ring. The hydroxyl substituent in position 4 may form an intramolecular O—H...N bond and in that way stabilize the non-chair conformation of the ring. However, the existence of such a conformation stabilized by an intramolecular hydrogen bond was established only in solution (Lyle, 1957; Brière, Lemaire, Rasset & Dunand, 1970; Cygler, Markowicz, Skolimowski & Skowroński, 1980).

In our earlier studies we have investigated 4-ethynyl-2,2,6,6-tetramethyl-4-piperidinol, TMPE (Cygler, Grabowski, Skolimowski & Skowroński, 1978), and 4-ethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, TMPEOx (Cygler, 1979). Both molecules exist in the solid state in a chair conformation. The ring is more distorted than in the case of 2,6-diaxial interactions only (*e.g.*, Ruben, Zalkin & Templeton, 1974; De Camp, Mićović & Pelletier, 1974) and shows the greatest flexibility at the methylene groups (positions 3 and 5). In both compounds the hydroxyl groups adopt equatorial positions and form strong intermolecular hydrogen bonds, which have some influence on the ring distortion (Cygler *et al.*, 1978).

To elucidate the effect of substituents at the N atom on the ring conformation we have studied the title compound (PMPE) with a methyl group in position 1.



Colourless, prismatic crystals were obtained by slow sublimation. The crystal (0.3 × 0.2 × 0.2 mm) chosen for X-ray measurements was sealed in a Lindemann capillary. Intensities were measured on a CAD-4 diffractometer at 253 K with monochromatized  $Cu K\alpha$

\* The Conformation of the Piperidine Ring. III. Part II: Cygler (1979).