

(2*R*,4*R*–2*S*,4*S*)-5,5-Dimethyl-4-phenyl-2-hexyl 3,5-Dinitrobenzoate

BY A. DE ANDRÉS,* J. L. BALCAZAR† AND J. FAYOS

Departamento de Rayos X, Instituto Rocasolano, Serrano 119, Madrid-6, Spain

(Received 21 January 1982; accepted 28 April 1982)

Abstract. C₂₁H₂₄N₂O₆, monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 14.549 (1), *b* = 11.195 (1), *c* = 13.694 (1) Å, β = 110.15 (2)°, *D*_x = 1.269 Mg m⁻³, *R* = 0.059 for 2700 observed reflexions. The conformations at the two chiral centres, separated by a methylene bridge, are compared with those theoretically predicted for the free carbinol.

Introduction. The conformations of acyclic racemates of diastereomers with two chiral centres separated by a methylene bridge have been studied by conformational energy calculations and proton NMR in compounds *r*(OH)HC–CH₂–CHPh r' with the radicals Ph, Me and Me₃ (Fernandez, Perez-Ossorio & Rico, 1974; Alvarez, Fernandez & Rico, 1975; Alvarez, Arias, Fernandez & Rico, 1977; Alvarez, Arias & Garcia, 1982). Each compound is a mixture of racemate isomers with different possible orientations of the substituents at the chiral centres. Each racemic isomer was separated by means of fractional recrystallization of their 3,5-dinitrobenzoates (DNB) in anhydrous methanol. The carbinols were liberated afterwards by saponification of the corresponding DNB derivatives. The crystal structure of (*R*,*R*–*S*,*S*)-Me₃C(DNB)HC–CH₂–CHPhCMe₃ (Andres, Balcazar, Martinez-Ripoll & Garcia-Blanco, 1981) confirms that this compound has the unique conformation predicted for its carbinol (Alvarez *et al.*, 1977), the torsions at both sides of the methylene bridge deviating by 10 and 34° with respect to the predicted staggered–staggered model. In this work, the crystal structure of (*R*,*R*–*S*,*S*)-Me(DNB)HC–CH₂–CHPhCMe₃ is compared with the theoretical model predicted for the free carbinol.

Intensities of 3765 independent reflexions were measured up to θ = 65° on a computer-controlled four-circle diffractometer. Graphite-monochromated Cu *K*α radiation (1.5418 Å) and the ω/2θ scan technique were used. No crystal decomposition was observed during the data collection. 2700 structure factors were considered as observed, *I* > 2σ(*I*). The structure was solved by *MULTAN* (Main, Lessinger,

Woolfson, Germain & Declercq, 1977) and refined by full-matrix least-squares analysis. All the H atoms were located on a difference map. A convenient weighting scheme was chosen to prevent trends in $w\Delta^2 F$ vs $\langle |F_o| \rangle$ and $\langle \sin \theta/\lambda \rangle$. Several cycles of weighted anisotropic refinement (fixed isotropic for H atoms) converged to *R* = 0.059 and *R*_w = 0.079 (Stewart, Kundell & Baldwin, 1970).

Discussion. Fig. 1 shows the molecular crystal structure of the *R*,*R* molecule. The positional and thermal parameters are given in Table 1, bond lengths and

Table 1. Fractional coordinates and thermal parameters as $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \cos(a_i, a_j)$ (Å² × 10⁴)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C(1)	0.4784 (1)	0.1336 (2)	0.8754 (2)	552 (8)
C(2)	0.4453 (1)	0.0995 (2)	0.7720 (2)	570 (8)
C(3)	0.5007 (2)	0.1279 (2)	0.7116 (2)	580 (8)
C(4)	0.5876 (2)	0.1901 (2)	0.7491 (2)	632 (9)
C(5)	0.6191 (2)	0.2202 (2)	0.8523 (2)	624 (8)
C(6)	0.5675 (2)	0.1925 (2)	0.9173 (2)	601 (8)
C(7)	0.4190 (2)	0.1094 (2)	0.9430 (2)	578 (8)
C(8)	0.2582 (2)	0.0529 (2)	0.9400 (2)	649 (9)
C(9)	0.2154 (2)	0.1729 (2)	0.9538 (2)	594 (9)
C(10)	0.1406 (1)	0.1639 (2)	1.0100 (2)	535 (8)
C(11)	0.1845 (1)	0.1075 (2)	1.1164 (2)	528 (8)
C(12)	0.2746 (2)	0.1431 (2)	1.1887 (2)	660 (9)
C(13)	0.3096 (2)	0.0927 (3)	1.2868 (2)	786 (11)
C(14)	0.2588 (3)	0.0055 (3)	1.3159 (2)	812 (12)
C(15)	0.1713 (3)	−0.0328 (3)	1.2459 (2)	811 (13)
C(16)	0.1351 (2)	0.0178 (3)	1.1469 (2)	670 (10)
C(17)	0.1855 (3)	−0.0331 (3)	0.8705 (3)	917 (14)
C(21)	0.0872 (2)	0.2859 (2)	1.0108 (2)	657 (10)
C(22)	0.0134 (2)	0.2692 (3)	1.0663 (3)	892 (15)
C(23)	0.1586 (2)	0.3852 (3)	1.0647 (3)	901 (15)
C(24)	0.0312 (3)	0.3238 (3)	0.8982 (3)	947 (15)
N(25)	0.7127 (2)	0.2853 (2)	0.8964 (2)	820 (10)
N(26)	0.4650 (2)	0.0910 (2)	0.6018 (2)	711 (8)
O(27)	0.3908 (2)	0.0313 (3)	0.5717 (2)	1283 (14)
O(28)	0.5118 (2)	0.1194 (2)	0.5479 (1)	888 (9)
O(29)	0.7487 (2)	0.3266 (3)	0.8353 (2)	1262 (14)
O(30)	0.7475 (1)	0.2967 (2)	0.9902 (2)	1055 (10)
O(31)	0.3288 (1)	0.0747 (2)	0.8870 (1)	660 (6)
O(32)	0.4495 (1)	0.1217 (2)	1.0365 (1)	711 (7)

* Permanent address: Instituto 'Elhuyar', CSIC, Serrano 119, Madrid-6, Spain.

† Permanent address: Departamento de Geología, Universidad de Alcalá de Henares, Spain.

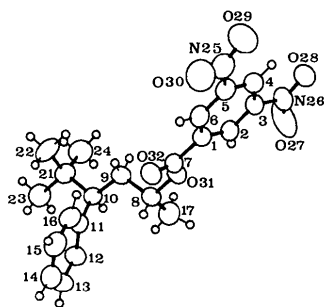


Fig. 1. X-ray molecular model of (*R,R*)-Me(DNB)HC-CH₂-CHPhCMe₃.

Table 2. Bond lengths (Å) and angles (°)

Averaged e.s.d.'s are 0.003 Å and 0.25°.

1-2	1.384	7-32	1.209	13-14	1.365
1-6	1.389	8-9	1.519	14-15	1.372
1-7	1.494	8-17	1.504	15-16	1.395
2-3	1.376	8-31	1.469	21-22	1.526
3-4	1.378	9-10	1.537	21-23	1.526
3-26	1.471	10-11	1.513	21-24	1.534
4-5	1.369	10-21	1.573	25-29	1.221
5-6	1.383	11-12	1.402	25-30	1.214
5-25	1.478	11-16	1.380	26-27	1.215
7-31	1.329	12-13	1.382	26-28	1.206
6-1-7	119.2	17-8-31	104.6	11-16-15	121.9
2-1-7	120.9	9-8-31	107.5	10-21-24	109.0
2-1-6	120.0	9-8-17	114.6	10-21-23	112.3
1-2-3	118.8	8-9-10	113.3	10-21-22	109.3
2-3-26	118.4	9-10-21	112.6	23-21-24	108.8
2-3-4	123.0	9-10-11	111.9	22-21-24	108.3
4-3-26	118.6	11-10-21	113.7	22-21-23	109.1
3-4-5	116.5	10-11-16	120.3	5-25-30	118.2
4-5-25	118.5	10-11-12	122.9	5-25-29	117.4
4-5-6	123.1	12-11-16	116.8	29-25-30	124.4
6-5-25	118.4	11-12-13	120.8	3-26-28	118.5
1-6-5	118.5	12-13-14	121.4	3-26-27	117.4
1-7-32	123.7	13-14-15	119.0	27-26-28	124.1
1-7-31	111.2	14-15-16	120.1	7-31-8	118.8
31-7-32	125.1				

angles in Table 2.* Table 3 shows some interesting torsional angles of the molecule. The conformation at

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36902 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Some torsional angles (°)

Averaged least-squares standard deviation is 0.3°. The C atoms are represented only by their ordinals.

4-3-N(26)-O(28)	-1.9	O(31)-8-9-10	-179.3
4-5-N(25)-O(29)	12.2	17-8-9-10	65.0
6-1-7-O(32)	-11.5	8-9-10-21	-172.6
O(32)-7-O(31)-8	2.2	8-9-10-11	57.9
7-O(31)-8-H(8)	-35.9	21-10-11-16	98.5
7-O(31)-8-9	82.5	9-10-21-22	179.2
7-O(31)-8-17	-155.4	9-8-17-H(173)	172

C(8) and C(10) deviates slightly, 1 and 7°, from the more populated (70%) conformation predicted by Alvarez *et al.* (1982) for the corresponding free carbinol.

We thank Professor S. García-Blanco and the Centro de Proceso de Datos del Ministerio de Educación y Ciencia, Madrid.

References

- ALVAREZ, C., ARIAS, M. S., FERNANDEZ, F. & RICO, M. (1977). *Org. Magn. Reson.* **10**, 251-254.
- ALVAREZ, C., ARIAS, M. S. & GARCIA, M. T. (1982). *Org. Magn. Reson.* In the press.
- ALVAREZ, C., FERNANDEZ, F. & RICO, M. (1975). *An. Quim.* **71**, 314-321.
- ANDRES, A., BALCAZAR, J. L., MARTÍNEZ-RIPOLL, M. & GARCÍA-BLANCO, S. (1981). *Acta Cryst.* **B37**, 772-774.
- FERNANDEZ, F., PEREZ-OSSORIO, R. & RICO, M. (1974). *An. Quim.* **70**, 524-532.
- MAIN, P., LESSINGER, L., WOLFFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. of York, England.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.