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Structures of *meso*- and (\pm)-1,2-Dinitro-1,2-diphenylethane and 2,3-Dinitro-2,3-diphenylbutane

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Abstract

The crystal and molecular structures of *meso*-1,2-dinitro-1,2-diphenylethane, C₁₄H₁₂N₂O₄, (1), (\pm)-1,2-dinitro-1,2-diphenylethane, C₁₄H₁₂N₂O₄, (2), *meso*-2,3-dinitro-2,3-diphenylbutane, C₁₆H₁₆N₂O₄, (3), and (\pm)-2,3-dinitro-2,3-diphenylbutane, C₁₆H₁₆N₂O₄, (4), have been determined by single-crystal X-ray diffraction methods. Compound (1): monoclinic, *P*2₁/*n*, *M*_r = 272.3, *a* = 5.597 (3), *b* = 8.185 (4), *c* = 14.389 (6) Å, β = 90.51 (2)°, *V* = 659.2 (6) Å³, *Z* = 2, *D*_x = 1.372 Mg m⁻³, Mo *K*α (λ = 0.71069 Å), μ = 0.096 mm⁻¹, *F*(000) = 284, *T* = 297 K, *R* = 0.051 for 604 reflections. Compound (2): monoclinic, *C*2/*c*, *M*_r = 272.3, *a* = 18.260 (5), *b* = 9.888 (3), *c* = 17.660 (4) Å, β = 119.40 (2)°, *V* = 2778.2 (13) Å³, *Z* = 8, *D*_x = 1.302 Mg m⁻³, Mo *K*α (λ = 0.71069 Å), μ = 0.091 mm⁻¹, *F*(000) = 1136, *T* = 297 K, *R* =

0.053 for 1000 reflections. Compound (3): monoclinic, *P*2₁/*n*, *M*_r = 300.3, *a* = 7.763 (2), *b* = 18.406 (3), *c* = 10.240 (2) Å, β = 90.10 (2)°, *V* = 1463.2 (5) Å³, *Z* = 4, *D*_x = 1.363 Mg m⁻³, Mo *K*α (λ = 0.71068 Å), μ = 0.099 mm⁻¹, *F*(000) = 632, *T* = 297 K, *R* = 0.033 for 1749 reflections. Compound (4): monoclinic, *C*2/*c*, *M*_r = 300.3, *a* = 17.928 (5), *b* = 8.713 (2), *c* = 12.366 (4) Å, β = 129.14 (2)°, *V* = 1498.2 (7) Å³, *Z* = 4, *D*_x = 1.331 Mg m⁻³, Mo *K*α (λ = 0.71069 Å), μ = 0.097 mm⁻¹, *F*(000) = 632, *T* = 297 K, *R* = 0.041 for 898 reflections. Compound (1) adopts a structure in which the two nitro groups are *trans* to each other. In compounds (2), (3) and (4) the two nitro groups are *gauche*. Contrary to normal expectation, (3) (the *meso* compound) has a lower melting point than (4) (the racemate). Semiempirical MO studies on the geometries and *gauche:trans* population distributions of these compounds in the gas phase are also reported.

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Table 1. Crystallographic data and experimental details for meso-1,2-dinitro-1,2-diphenylethane (1), (\pm)-1,2-dinitro-1,2-diphenylethane (2), meso-2,3-dinitro-2,3-diphenylbutane (3) and (\pm)-2,3-dinitro-2,3-diphenylbutane (4)

| | (1) (<i>meso</i>) | (2) (\pm) | (3) (<i>meso</i>) | (4) (\pm) |
|---|---|---|--|--|
| Crystal size (mm) | 0.35 \times 0.30 \times 0.25 | 0.45 \times 0.35 \times 0.30 | 0.35 \times 0.30 \times 0.25 | 0.35 \times 0.30 \times 0.25 |
| Diffractometer | Siemens R3m/V | Siemens R3m/V | Siemens R3m/V | Siemens R3m/V |
| Monochromator | Graphite | Graphite | Graphite | Graphite |
| Data-collection range ($^{\circ}$) | 3 < 2 θ < 48 | 0 < 2 θ < 48 | 0 < 2 θ < 50 | 3 < 2 θ < 50 |
| Scan width ($^{\circ}$) | 2.00 | 2.00 | 1.20 | 1.20 |
| Range of <i>hkl</i> | <i>h</i> 0 to 6 <i>k</i> -9 to 9 <i>l</i> -16 to 16 | <i>h</i> 0 to 18 <i>k</i> 0 to 6 <i>l</i> -18 to 17 | <i>h</i> -9 to 9 <i>k</i> 0 to 20 <i>l</i> 0 to 12 | <i>h</i> -21 to 16 <i>k</i> 0 to 10 <i>l</i> 0 to 14 |
| Absorption correction | None | None | None | None |
| Standard reflections | 120, 202, 111 | 420, 131, 241 | 052, 024, 262 | 623, 020, 310 |
| Intensity variation (%) | \pm 1.5 | \pm 1.5 | \pm 1.5 | \pm 1.5 |
| No. of reflections measured | 2306 | 1800 | 2829 | 1491 |
| No. of unique reflections | 1035 | 1606 | 2578 | 1328 |
| No. of reflections used [$I > 2\sigma(I)$] | 604 | 1000 | 1749 | 898 |
| Final number of variables | 99 | 182 | 200 | 101 |
| R_{int} (%) | 2.81 | 1.61 | 1.20 | 1.88 |
| wR (%) | 4.70 | 4.30 | 3.58 | 4.56 |
| R (%) | 5.31 | 5.34 | 3.33 | 4.14 |
| Weighting constants g, k [$w = g/(\sigma^2 F_o + kF_o^2)$] | 1, 3 $\times 10^{-4}$ | 1, 3 $\times 10^{-4}$ | 1, 5 $\times 10^{-4}$ | 1, 5 $\times 10^{-4}$ |
| Maximum shift/e.s.d | 0.034 | 0.013 | 0.070 | 0.014 |
| Peaks in final map (e \AA^{-3}) | 0.14, -0.14 | 0.17, -0.19 | 0.14, -0.12 | 0.15, -0.14 |
| S | 1.89 | 1.79 | 1.13 | 1.46 |
| No. and range of reflections used for unit-cell determination | | 20 reflections (6 < 2 θ < 21 $^{\circ}$) for all four cases | | |

Introduction

In a previous physico-chemical study on the rotational isomerism of the title compounds (Chia, Tan & Huang, 1989), it was assumed, following common practice, that for a diastereoisomeric pair, the compound with the higher melting point may be assigned the *meso* and that with the lower melting point the (\pm) configuration. As there is no *a priori* reason why this should always be true, it was thought desirable to determine the stereostructures of the title compounds to put the work cited on a firmer base. In this paper we report the crystal structures by X-ray diffraction and the results of semiempirical MO studies on the geometries and *gauche:trans* population distributions in the gas phase of the symmetrically substituted dinitroethanes: *meso*-1,2-dinitro-1,2-diphenylethane (1), (\pm)-1,2-dinitro-1,2-diphenylethane (2), *meso*-2,3-dinitro-2,3-diphenylbutane (3) and (\pm)-2,3-dinitro-2,3-diphenylbutane (4). These compounds differ in substitution only in respect of H *versus* Me on the central C atoms.

Experimental

Compounds (1) to (4) were prepared as described earlier (Chia, Tan & Huang, 1989). X-ray data were collected on a Siemens R3m/V 2000 diffractometer and corrected for Lorentz and polarization factors. All four structures were solved by direct methods and refined (on F) by full-matrix least-squares analysis using *SHELXTL-Plus* (Siemens Analytical X-ray Instruments Inc., 1989). Scattering factors were ob-

tained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Non-H atoms were refined anisotropically except for the disordered C atoms [C(1), C(1x), C(1y), C(1z)] in compound (1) which were refined isotropically. H atoms were located from difference maps or placed on calculated positions with fixed isotropic thermal parameters. Details of the data collection and structure refinements are given in Table 1 and non-H atomic coordinates are listed in Tables 2-5.* Selected bond lengths, bond angles and torsion angles are given in Table 6. The atomic nomenclature is defined in Figs. 1(a)-1(d). Thermal ellipsoids were drawn at the 35% probability level. Compound (3) has a β value of 90.10 (2) $^{\circ}$. However, the intensity data clearly indicated a monoclinic cell. Forcing the cell to become orthorhombic resulted in $R_{\text{int}} > 0.20$. The results of final refinement confirmed that the cell is monoclinic. For compounds (1) and (3), $P2_1/c$ was not chosen as β would be too far from 90 $^{\circ}$. The widely accepted $P2_1/n$ was used instead.

Semiempirical MO calculations were performed using the program *AMPAC2.1* (Dewar, Zoebisch, Healy & Stewart, 1986). *AM1* (Dewar, Zoebisch, Healy & Stewart, 1985) and *MNDO* (Dewar & Thiel, 1977) parametrizations were used with full geometry

* Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55480 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1009]

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for meso-1,2-dinitro-1,2-diphenylethane

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | x | y | z | U_{eq} | S.o.f.* |
|-------|-----------|-----------|-----------|----------|---------|
| N(1) | 1698 (6) | -1986 (3) | 3 (2) | 65 (1) | 1 |
| O(1) | 414 (5) | -3120 (3) | -31 (3) | 108 (1) | 1 |
| O(2) | 3824 (5) | -2035 (3) | 2 (2) | 97 (1) | 1 |
| C(1) | 1026 (15) | -213 (12) | 312 (7) | 55 (2) | 0.40 |
| C(1x) | -302 (30) | -704 (22) | 311 (13) | 54 (4) | 0.22 |
| C(1y) | 1027 (27) | -224 (21) | -323 (12) | 53 (4) | 0.23 |
| C(1z) | -292 (45) | -702 (33) | -338 (19) | 58 (6) | 0.15 |
| C(11) | 91 (8) | -73 (5) | 1339 (3) | 87 (2) | 1 |
| C(12) | -1716 (7) | -818 (5) | 1811 (3) | 87 (2) | 1 |
| C(13) | -1763 (7) | -816 (5) | 2746 (3) | 84 (2) | 1 |
| C(14) | -10 (8) | -55 (5) | 3240 (3) | 83 (2) | 1 |
| C(15) | 1781 (7) | 693 (4) | 2775 (3) | 85 (2) | 1 |
| C(16) | 1844 (7) | 684 (4) | 1846 (3) | 88 (2) | 1 |

*S.o.f. = site occupation factor.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for (\pm)-1,2-dinitro-1,2-diphenylethane

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | x | y | z | U_{eq} |
|-------|----------|----------|----------|----------|
| C(1) | 3210 (2) | 1424 (4) | 3456 (2) | 58 (2) |
| C(2) | 4116 (2) | 1595 (4) | 4153 (2) | 55 (2) |
| C(11) | 3111 (2) | 953 (5) | 2593 (2) | 55 (2) |
| C(12) | 2597 (3) | 1668 (5) | 1858 (3) | 77 (3) |
| C(13) | 2479 (3) | 1239 (7) | 1062 (3) | 103 (4) |
| C(14) | 2867 (4) | 108 (7) | 1005 (3) | 97 (4) |
| C(15) | 3382 (3) | -611 (5) | 1732 (3) | 91 (3) |
| C(16) | 3505 (3) | -189 (5) | 2528 (3) | 74 (3) |
| C(21) | 4541 (3) | 2748 (6) | 3965 (2) | 54 (3) |
| C(22) | 4243 (3) | 4038 (7) | 3876 (3) | 71 (3) |
| C(23) | 4647 (3) | 5089 (6) | 3715 (3) | 84 (3) |
| C(24) | 5327 (4) | 4839 (8) | 3623 (3) | 96 (4) |
| C(25) | 5627 (3) | 3548 (9) | 3707 (3) | 100 (4) |
| C(26) | 5235 (3) | 2502 (6) | 3875 (3) | 78 (3) |
| N(1) | 2771 (3) | 390 (5) | 3740 (3) | 80 (3) |
| N(2) | 4161 (3) | 1855 (4) | 5030 (2) | 69 (2) |
| O(1) | 2028 (3) | 519 (5) | 3427 (3) | 135 (3) |
| O(2) | 3207 (3) | -494 (4) | 4240 (2) | 107 (3) |
| O(3) | 4802 (2) | 1499 (3) | 5671 (2) | 104 (2) |
| O(4) | 3577 (2) | 2433 (3) | 5032 (2) | 84 (2) |

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for meso-2,3-dinitro-2,3-diphenylbutane

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | x | y | z | U_{eq} |
|-------|-----------|----------|-----------|----------|
| C(10) | 1253 (3) | 6832 (1) | 3735 (2) | 63 (1) |
| C(1) | 436 (2) | 6421 (1) | 2600 (2) | 43 (1) |
| C(2) | -570 (2) | 6955 (1) | 1655 (2) | 43 (1) |
| C(20) | -1813 (3) | 7421 (1) | 2463 (2) | 63 (1) |
| C(11) | -743 (2) | 5800 (1) | 3066 (2) | 39 (1) |
| C(12) | -1498 (3) | 5832 (1) | 4291 (2) | 56 (1) |
| C(13) | -2558 (3) | 5281 (1) | 4717 (2) | 69 (1) |
| C(14) | -2891 (2) | 4689 (1) | 3947 (2) | 62 (1) |
| C(15) | -2152 (2) | 4649 (1) | 2738 (2) | 56 (1) |
| C(16) | -1090 (2) | 5197 (1) | 2295 (2) | 47 (1) |
| C(21) | -1520 (2) | 6612 (1) | 495 (2) | 40 (1) |
| C(22) | -3148 (2) | 6323 (1) | 685 (2) | 50 (1) |
| C(23) | -4045 (3) | 6004 (1) | -326 (2) | 61 (1) |
| C(24) | -3350 (3) | 5981 (1) | -1551 (2) | 65 (1) |

Table 4 (cont.)

| | x | y | z | U_{eq} |
|-------|-----------|----------|-----------|----------|
| C(25) | -1756 (3) | 6279 (1) | -1769 (2) | 59 (1) |
| C(26) | -844 (2) | 6592 (1) | -758 (2) | 48 (1) |
| N(1) | 1925 (2) | 6032 (1) | 1870 (2) | 52 (1) |
| N(2) | 729 (3) | 7506 (1) | 1061 (2) | 57 (1) |
| O(1) | 1711 (2) | 5849 (1) | 742 (1) | 65 (1) |
| O(2) | 3214 (2) | 5888 (1) | 2494 (2) | 79 (1) |
| O(3) | 2255 (2) | 7370 (1) | 1038 (2) | 76 (1) |
| O(4) | 120 (2) | 8059 (1) | 608 (2) | 92 (1) |

Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for (\pm)-2,3-dinitro-2,3-diphenylbutane

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | x | y | z | U_{eq} |
|-------|----------|----------|----------|----------|
| C(10) | 1027 (2) | 1609 (3) | 4549 (2) | 55 (1) |
| C(1) | 571 (1) | 1398 (2) | 3019 (2) | 42 (1) |
| C(11) | 958 (1) | 2590 (2) | 2571 (2) | 45 (1) |
| C(12) | 1176 (2) | 2231 (3) | 1707 (3) | 64 (2) |
| C(13) | 1521 (2) | 3323 (4) | 1320 (3) | 81 (2) |
| C(14) | 1648 (2) | 4781 (4) | 1768 (3) | 80 (2) |
| C(15) | 1432 (2) | 5192 (3) | 2613 (3) | 75 (2) |
| C(16) | 1096 (2) | 4090 (3) | 3035 (2) | 58 (2) |
| N(1) | 928 (2) | -174 (2) | 2910 (2) | 56 (1) |
| O(1) | 418 (1) | -881 (2) | 1824 (2) | 75 (1) |
| O(2) | 1724 (1) | -588 (2) | 3914 (2) | 86 (1) |

Table 6. Selected bond lengths (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$)

| | (1) | (2) | (3) | (4) |
|-----------------------|------------|------------|-----------|------------|
| C(1)—C(2) | 1.493 (18) | 1.510 (5) | 1.585 (2) | 1.589 (4) |
| C(1)—C(11) | 1.577 (10) | 1.516 (6) | 1.540 (2) | 1.534 (4) |
| C(2)—C(21) | 1.577 (10) | 1.504 (6) | 1.532 (2) | 1.534 (4) |
| N(1)—C(1) | 1.564 (10) | 1.528 (8) | 1.553 (2) | 1.554 (3) |
| N(1)—O(1) | 1.174 (4) | 1.194 (7) | 1.214 (2) | 1.212 (3) |
| N(1)—O(2) | 1.191 (4) | 1.219 (6) | 1.216 (2) | 1.212 (2) |
| N(2)—C(2) | 1.564 (10) | 1.533 (6) | 1.555 (2) | 1.554 (3) |
| N(2)—O(3) | 1.174 (4) | 1.214 (4) | 1.211 (2) | 1.212 (3) |
| N(2)—O(4) | 1.191 (4) | 1.210 (6) | 1.214 (2) | 1.212 (2) |
| C(1)—C(10) | - | - | 1.524 (3) | 1.525 (3) |
| C(2)—C(20) | - | - | 1.534 (3) | 1.525 (3) |
| O(1)—N(1)—C(1) | 126.6 (4) | 115.9 (4) | 119.0 (1) | 118.7 (2) |
| O(2)—N(1)—C(1) | 105.9 (4) | 117.2 (5) | 117.4 (2) | 117.1 (2) |
| O(1)—N(1)—O(2) | 125.8 (3) | 126.9 (6) | 123.4 (2) | 124.1 (2) |
| C(16)—C(11)—C(1) | 106.9 (5) | 121.8 (4) | 122.2 (1) | 119.5 (3) |
| N(1)—C(1)—C(2) | 103.4 (9) | 110.4 (3) | 111.0 (1) | 108.7 (1) |
| C(11)—C(1)—C(2) | 106.6 (9) | 113.3 (4) | 110.9 (1) | 110.7 (2) |
| O(3)—N(2)—O(4) | 125.8 (3) | 125.6 (5) | 123.1 (2) | 124.1 (2) |
| N(2)—C(2)—C(1) | 103.4 (9) | 109.6 (4) | 108.9 (1) | 108.7 (1) |
| N(1)—C(1)—C(11) | 114.6 (6) | 107.5 (3) | 104.5 (1) | 105.1 (2) |
| C(21)—C(2)—N(2) | 114.6 (6) | 108.6 (3) | 106.1 (1) | 105.1 (2) |
| C(21)—C(2)—C(1) | 106.6 (9) | 112.5 (3) | 117.0 (1) | 110.7 (2) |
| C(10)—C(1)—C(2) | - | - | 111.2 (1) | 114.3 (3) |
| C(10)—C(1)—N(1) | - | - | 106.7 (1) | 106.6 (2) |
| C(10)—C(1)—C(11) | - | - | 112.3 (1) | 110.9 (2) |
| C(1)—C(2)—C(20) | - | - | 109.1 (1) | 114.3 (2) |
| C(20)—C(2)—N(2) | - | - | 104.8 (1) | 106.6 (2) |
| O(2)—N(1)—C(1)—C(2) | 139.1 (7) | -28.4 (6) | 147.1 (2) | -155.1 (2) |
| C(2)—C(1)—C(11)—C(12) | 58.7 (7) | -127.7 (4) | -99.9 (2) | -92.5 (2) |
| N(1)—C(1)—C(2)—N(2) | 180 | -50.6 (5) | -56.5 (2) | -42.8 (2) |
| N(1)—C(1)—C(2)—C(21) | -58.8 (7) | -171.4 (4) | 63.7 (2) | 157.8 (2) |
| C(1)—C(2)—C(21)—C(22) | -58.7 (7) | 59.5 (5) | 82.9 (2) | 92.5 (2) |
| C(1)—C(2)—N(2)—O(3) | 55.1 (7) | 152.3 (4) | 20.7 (2) | 27.6 (2) |
| C(11)—C(1)—C(2)—C(21) | 180 | 67.9 (5) | -52.0 (2) | -87.2 (2) |
| C(2)—C(1)—N(1)—O(1) | -55.1 (7) | 153.4 (5) | -37.2 (2) | 27.6 (2) |
| C(10)—C(1)—C(2)—C(20) | - | - | -51.7 (2) | 164.8 (2) |

optimization for each incremental value of the ethane C—C torsion angle. Torsion angles were defined by the atoms N—C—C—N using the convention of Klyne and Prelog (Klyne & Prelog, 1960). Calculations were performed on a VAX 8650 computer using FORTRAN77 operating under VMS.

Results and discussion

Crystallographic data for compounds (1)–(4) are given in Table 1 together with the experimental details. The *gauche* and *trans* rotamers expected for the title compounds are shown in Newmann projections in Fig. 2.

meso-1,2-Dinitro-1,2-diphenylethane (1)

The X-ray diffraction results confirm that the compound with the higher melting point (512–

513 K) is the *meso* isomer and that with the lower melting point (426–427 K) the racemic form.

In the *meso* isomer, all the substituent groups are *trans* to each other. However, there were problems in locating the two central C atoms. The asymmetric unit contained only half a molecule. Direct methods yielded the positions of all non-H atoms except the central C atoms. The initial positions of the central carbons, which were located from the difference map, led to a very short C(1)—C(2) central bond (1.1 Å) and a very long (1.7 Å) C—Ph bond, as well as extremely large thermal parameters for the central C atoms. Disorder was therefore suspected. A disordered model with the central C atoms at two positions reduced the *R* value from 0.082 to 0.065. However, the bond lengths and thermal parameters thus obtained were still unsatisfactory. With the help of electron density maps, a four-site disordered model for the central C atoms with occupancies of

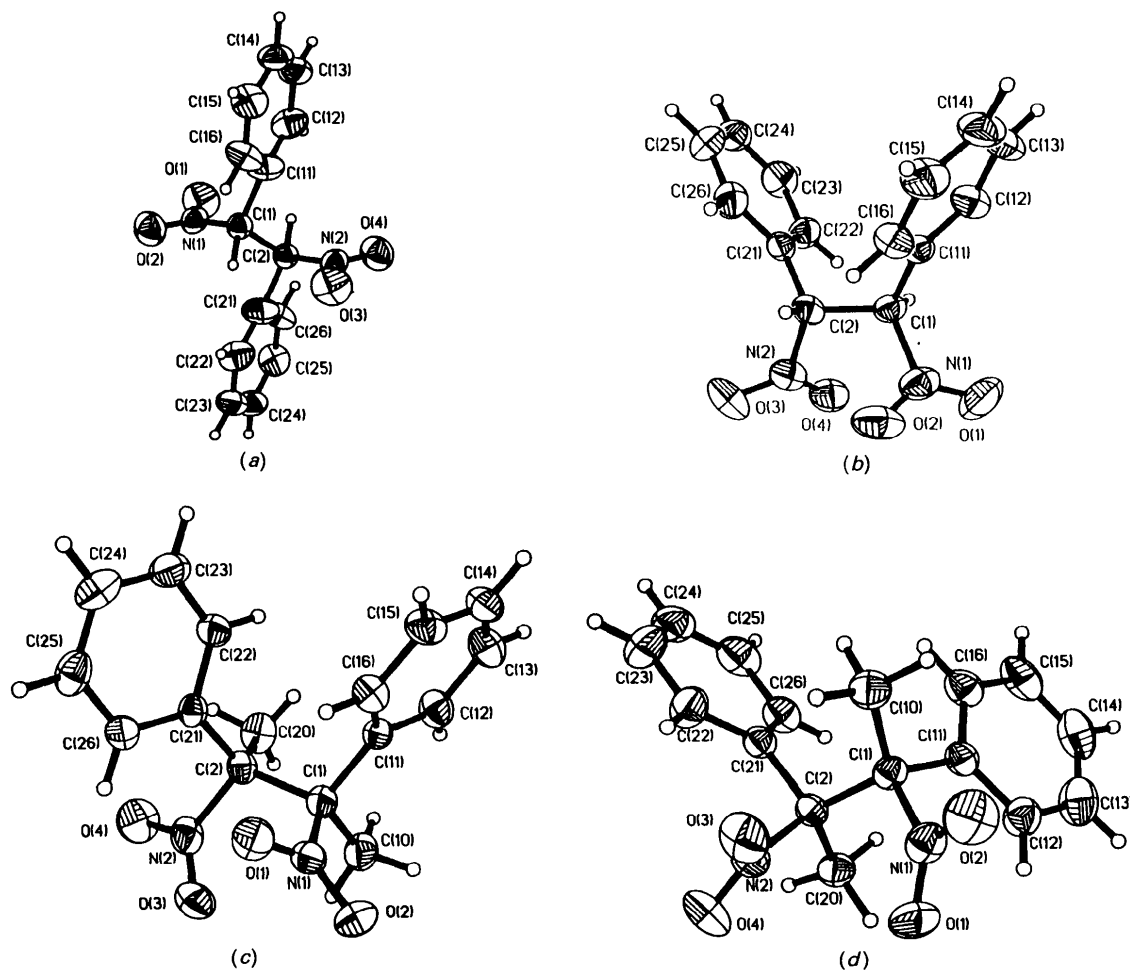


Fig. 1. Atomic numbering and thermal-ellipsoid plots at 35% probability level. Thermal ellipsoid diagrams of (a) *meso*-1,2-dinitro-1,2-diphenylethane, (b) (±)-1,2-dinitro-1,2-diphenylethane, (c) *meso*-2,3-dinitro-2,3-diphenylbutane, (d) (±)-2,3-dinitro-2,3-diphenylbutane.

0.40:0.22:0.23:0.15 and isotropic thermal parameters gave a final R value of 0.053 and wR of 0.044. The bond lengths and thermal parameters of the disordered C atoms also settled down to within expected ranges. This model gives the molecule a centre of symmetry and results in an overall *trans* conformation with an average central C(1)—C(2) bond length of 1.52 (2) Å and C—Ph bond length of 1.59 (2) Å. Other atoms including the two H atoms bonded to the central C atoms are ordered. The two phenyl rings are coplanar and are perpendicular to the two nitro groups which are also coplanar. As a result of this perpendicular arrangement, and because the monoclinic β angle is close to 90°, the molecules can be packed together so that all the nitro groups are aligned close to a plane perpendicular to the c axis of the unit cell whereas the phenyl groups are coplanarly aligned, in two groups, along the c axis. The packing is therefore efficient despite the disorder. The C(1)—C(2), N—C and C—Ph bonds are all longer than those in the (\pm) compound (Table 6), as may be expected because of the disorder forced by the crystal packing. Other bond lengths and angles are more normal: the average phenyl ring C—C bond is 1.36 (2) Å, the N—O bond length 1.18 (1) Å and the O—N—O angle 125.7 (3)°.

Both AM1 and MNDO calculations using the AMPAC2.1 program with full geometry optimization starting from the solid-state structure predict that the compound should be almost exclusively in the *trans* conformation in the gas phase (see Fig. 3). This is in good agreement with the *gauche:trans* population ratio of 11:89 in benzene solution deduced from dipole-moment measurements at

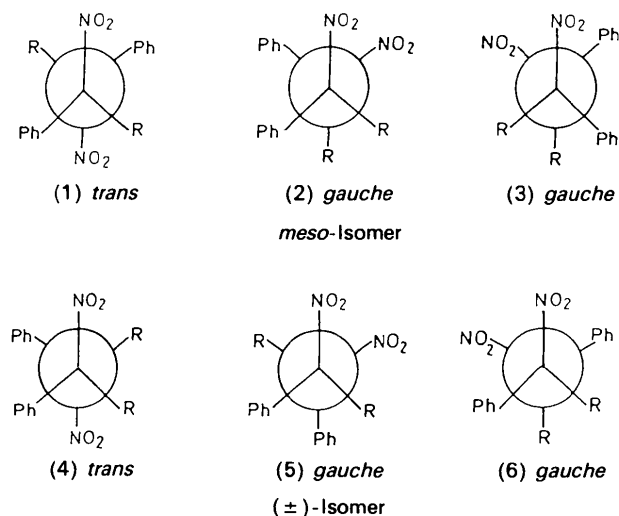


Fig. 2. Newman projections for the *trans* and *gauche* conformers of *meso*- and (\pm)- (a) 1,2-dinitro-1,2-diphenylethane ($R = H$) and (b) 2,3-dinitro-2,3-diphenylbutane ($R = CH_3$).

298 K (Chia, Tan & Huang, 1989). The fact that compound (1) adopts a *trans* structure in the solid state rather than *gauche* is in striking contrast to all the vicinal dinitroethanes studied so far (Kai, Knochel, Kwiatkowski, Dunitz, Oth, Seebach & Kalinowski, 1982; Lam, Huang & Hambley, 1990). In all these other instances the two nitro groups have invariably been found to be *gauche* to each other in the solid state (Kai, Knochel, Kwiatkowski, Dunitz, Oth, Seebach & Kalinowski, 1982; Lam, Huang & Hambley, 1990; Huang & co-workers, unpublished data). The *gauche* rotamer also tends to predominate in solution (Tan, Chia, Huang, Kuok & Tang, 1984; Tan, Chia & Huang, 1986; Lam, Tan & Huang, 1990; Tan, Lam, Huang & Chia, 1990). This preference for the *gauche* conformation has been attributed to the so-called *gauche* effect (Wolfe, 1972) which postulates that the structure which has the maximum number of *gauche* interactions between the adjacent electron pairs and/or polar bonds will be favoured. In addition to being highly polar, the nitro group possesses two electron pairs on each O atom and one electron pair on the N atom. It is therefore a substituent with unusually favourable properties for inducing the display of the *gauche* effect. However, in the case of *meso*-1,2-dinitro-1,2-diphenylethane, the dominant influence of this effect on conformation appears to have been offset by some other factor(s). One possible offsetting factor that needs to be considered is the intramolecular attraction that should exist at van der Waals distances between the H and Ph and between H and NO₂, caused by the acidic nature of the H atoms attached to the central C—C bond (Reutov, Beletskaya & Butin, 1978), the electron-deficient hydrogens being attracted by electron-rich groups such as nitro and phenyl. Support for this hypothesis can be found in our MO

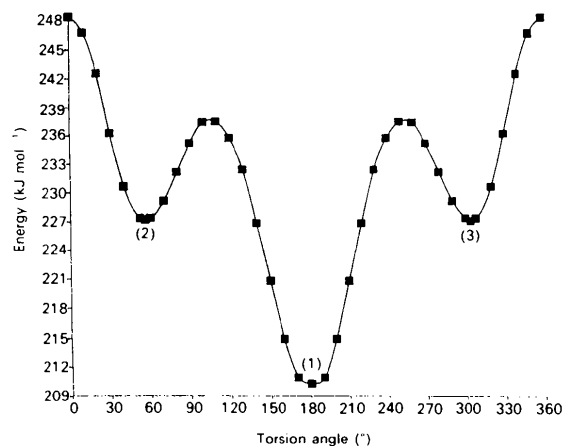


Fig. 3. Energy of *meso*-1,2-dinitro-1,2-diphenylethane as a function of the N—C—C—N torsion angle calculated using AM1 parametrization.

calculations. Indeed, an analysis of the intramolecular non-bonded interaction energies calculated with AM1 parametrization show that such attractions are not only predicted, but are also maximized in the *trans* rotamer, thus suggesting these to be the main cause of the *trans* being more stable than the *gauche* rotamer.

(±)-1,2-Dinitro-1,2-diphenylethane (2)

Each asymmetric unit of the unit cell contains one molecule. There are therefore four pairs of (+) and (-) molecules per cell. The molecule as a whole adopts the conformation shown as (5) in Fig. 2 where the nitro groups are *gauche* with an N(1)—C(1)—C(2)—N(2) torsion angle of -50.6 (5)°. In this conformation, the phenyl groups are also *gauche* with the C(11)—C(1)—C(2)—C(21) angle at 67.9 (5)° while the two H atoms are *trans* to each other. The central C(1)—C(2) bond length is 1.510 (5) Å and the average of the C(1)—Ph and C(2)—Ph bond lengths is 1.510 (6) Å. The average phenyl ring C—C bond is normal at 1.369 (9) Å as are the C—N bond [1.530 (8) Å], N—O bond [1.209 (6) Å] and O—N—O angle [126.3 (5)°]. The angle of orientation between the planes of the two phenyl rings is 72.3 (6)° and that between the planes of the two nitro groups is 64.1 (6)°. The ratio of the density of (1) to (2) is 1.054 indicating that compound (1) has more efficient packing than (2).

The distribution in the gas phase of the rotamers in any racemic compound of the type shown in Fig. 2 is governed by the Boltzmann-type equation:

$$(5):(4):(6) = \exp(-\Delta U_1/RT):1:\exp(-\Delta U_2/RT),$$

where $\Delta U_1 = U_{g_1} - U_t$ and $\Delta U_2 = U_{g_2} - U_t$, the symbols *g* and *t* referring to *gauche* and *trans*. For compound (2), AMPAC2.1 calculations predict that the *gauche* species (5) in Fig. 2 is the most stable rotamer, occurring to an extent of 69% (AM1) to 99% (MNDO). This is consistent with the structure (5) found in the solid state and also with the very high solution dipole-moment value of 20.05×10^{-30} C m in carbon tetrachloride solution at 298 K (Chia, Tan & Huang, 1989). The relative stabilities of the rotamers according to the AM1 parametrization are shown in the energy profile in Fig. 4.

meso-2,3-Dinitro-2,3-diphenylbutane (3)

The X-ray results show that the general practice of assigning the compound with higher melting point to the *meso* isomer and that with the lower melting point to the (±) isomer, in a diastereoisomeric pair, is *not* applicable here. The correct assignment for 2,3-dinitro-2,3-diphenylbutane is: the lower melting compound (411–413 K) is the *meso* isomer and the higher melting compound (420–421 K) the racemate.

The discussion on some of the physical data presented on these two compounds in our earlier study (Chia, Tan & Huang, 1989) therefore needs to be revised. In particular the IR and Raman data for the solids have been partly misinterpreted.

In compound (3), each asymmetric unit of the unit cell contains one molecule. The conformation adopted is one in which the two nitro groups are *gauche* [(2) or (3) in Fig. 2] with an N(1)—C(1)—C(2)—N(2) torsion angle of -56.5 (2)°. In this configuration, the phenyl and methyl substituent groups are also at *gauche* positions with the C(11)—C(1)—C(2)—C(21) and C(10)—C(1)—C(2)—C(20) torsion angles being -52.0 (2) and -51.7 (2)° respectively. Unlike compound (1), the two phenyl rings and the two nitro groups in compound (3) are no longer positioned in a coplanar fashion to each other but are instead oriented at angles of 34.0 (2) and 80.6 (2)° respectively to each other.

After least-squares refinements, the molecule showed a central C(1)—C(2) bond [1.585 (2) Å] which is much longer than that in (1) [1.520 (2) Å]. The C—Ph bond length of 1.536 (4) Å while compatible with the standard value of 1.544 Å, is significantly longer than the X-ray values of 1.50 and 1.527 Å obtained in dibenzyl (Cruickshank, 1949) and 1,2-diphenyltetrafluoroethane (Cruickshank, Jeffrey & Nyburg, 1959). This lengthening of bonds in *meso*-2,3-dinitro-2,3-diphenylbutane is consistent with the increased steric crowding expected about the central C atoms on substitution of the bulkier methyl groups.

The *gauche* conformation adopted by (3) in the solid is in striking contrast to the *trans* conformation found in (1). This may be explained as follows. In compound (3), the H atoms of the methyl groups are not as acidic as the single hydrogens in compound

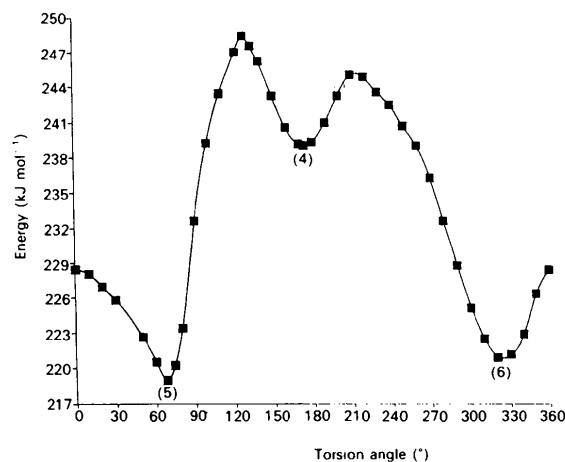


Fig. 4. Energy of (±)-1,2-dinitro-1,2-diphenylethane as a function of the N—C—C—N torsion angle calculated using AM1 parametrization.

(1) directly attached to the central C(1)—C(2) bond. We should therefore expect much weaker intramolecular attraction between the methyl hydrogens and the phenyl rings of (3). Thus, with the factor favouring the *trans* conformation in compound (1) largely diminished, compound (3) is free to adopt the alternative (*gauche*) conformation dictated by the influence of two vicinal nitro groups. AMPAC2.1 calculations with MNDO parametrization show that the *gauche* rotamer (2) or (3) in Fig. 2 is indeed more stable than the *trans*, predicting a *gauche:trans* ratio of 83:17 in the gas phase. This compares well with the ratio of 88:12 deduced from the dipole-moment value of 17.48×10^{-30} C m found in CCl₄ solution at 298 K (Chia, Tan & Huang, 1989). However, the AM1 parametrization gave a *gauche:trans* ratio of 11:89 (Fig. 5). This discrepancy is unexpected as

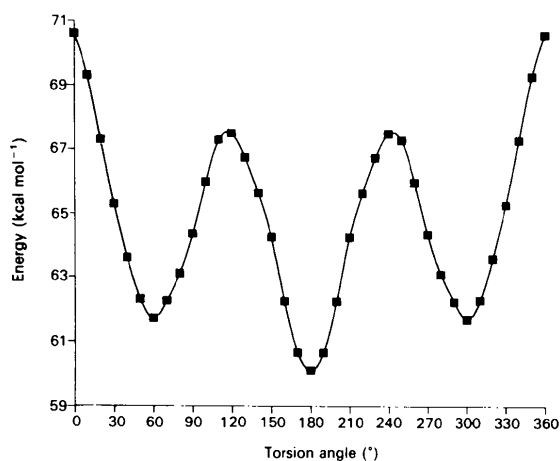


Fig. 5. Energy of *meso*-2,3-dinitro-2,3-diphenylbutane as a function of the N—C—C—N torsion angle calculated using AM1 parametrization. 1 kcal mol⁻¹ = 4.18 kJ mol⁻¹.

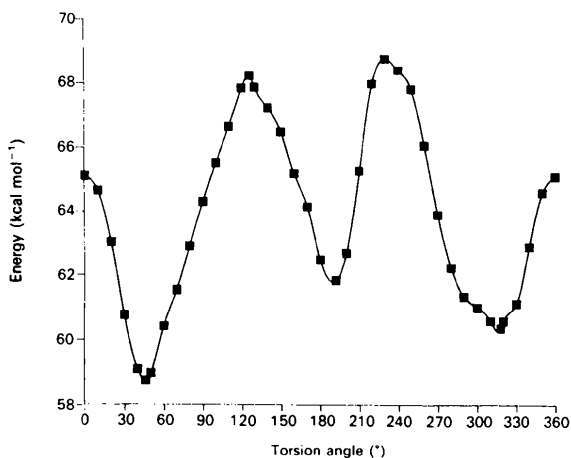


Fig. 6. Energy of (±)-2,3-dinitro-2,3-diphenylbutane as a function of the N—C—C—N torsion angle calculated using AM1 parametrization. 1 kcal mol⁻¹ = 4.184 kJ mol⁻¹.

application of AM1 parametrization to symmetrical dinitroethanes has so far shown good agreement with experiment (Tan, Lam, Huang & Chia, 1990; Lam, Tan & Huang, 1990; Lam, Koh & Huang, 1992). It could partly be due to an overestimation of the core-core repulsion energy terms in AM1, but could also be due in part to the errors inherent in the AM1 MO method of calculation [up to 5 kJ mol⁻¹ as suggested by Table 8 of Dewar, Zoebisch, Healy & Stewart (1985)]. In the case of compound (3), this is comparable to the rotamer energy difference implied by the observed *gauche:trans* ratio.

(±)-2,3-Dinitro-2,3-diphenylbutane (4)

Each asymmetric unit of the unit cell contains half a molecule. The molecule is located with its centre on the twofold axis. The structure of (4) in the crystalline state corresponds to rotamer (5) in Fig. 2 where the nitro groups are again *gauche*, with an N(1)—C(1)—C(2)—N(2) torsion angle of 42.8 (2)°. In this conformation the phenyl groups are also *gauche* with a torsion angle of -87.2 (2)° while the methyl groups are *trans* to each other. Furthermore, the planes of two phenyl rings are oriented at 25.2 (2)° with respect to each other while the planes of the two nitro groups are inclined at 59.7 (2)°. The final values of the central C(1)—C(2) bond of 1.589 (4) Å and the C—Ph, C—N and C—Me bonds of 1.534 (4), 1.554 (3) and 1.525 (3) Å respectively are comparable with those in compound (3). The C—C bond lengths in the benzene rings are also equal within experimental error to the values of the *meso* isomer.

The ratio of the density of the *meso* to (±) isomers of 2,3-dinitro-2,3-diphenylbutane is 1.024. Thus, as in 1,2-dinitro-1,2-diphenylethane, the *meso* isomer exhibits slightly more efficient packing than its (±) modification.

Both AM1 and MNDO calculations agree to within 3% in predicting a population distribution of 6:93:1 for (6):(5):(4) (Fig. 6). Again this is consistent with the high dipole-moment value of 20.35×10^{-30} C m observed in carbon tetrachloride solution at 298 K (Chia, Tan & Huang, 1989). The far greater stability of (5) is also consistent with the fact that the structure found by X-ray diffraction turns out to be rotamer (5).

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Molecular Structures of L-Leu-L-Tyr, Gly-D,L-Met-*p*-Toluenesulfonate and L-His-L-Leu

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Abstract

L-Leu-L-Tyr, (I), $C_{15}H_{22}N_2O_4$, $M_r = 294.35$, crystallizes from MeOH/5% dimethyl sulfoxide in the orthorhombic space group $P2_12_12_1$. $a = 5.644$ (1), $b = 12.094$ (3), $c = 22.548$ (4) Å, $V = 1539.0$ (5) Å³, $Z = 4$, $D_x = 1.270$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.54184$ Å, $\mu = 7.228$ cm⁻¹, $F(000) = 632$, $T = 173$ K, final R (on F) = 0.033 for 1347 observations with $I \geq 2\sigma(I)$. (I) crystallizes as a zwitterion with the N-terminus protonated and the C-terminus ionized. The peptide backbone adopts a distorted *trans* antiparallel β pleated-sheet conformation, with principal torsion angles $\psi_1 = 163.7$ (2), $\omega_1 = 158.7$ (2), $\varphi_2 = -110.9$ (3) and $\psi_2 = 141.4$ (2)°. The leucyl residue is in the $g^-(tg^-)$ conformation while the tyrosyl residue adopts the g^- conformation, with the phenol ring twisted from the low-energy perpendicular position. Gly-D,L-Met-*p*-toluenesulfonate, (II), $C_7H_{15}N_2O_3S^+ \cdot C_7H_7O_3S^-$, $M_r = 378.47$, crystallizes from MeOH/EtOAc in the orthorhombic space group $Pbca$. $a = 33.642$ (4), $b = 15.951$ (1), $c = 6.785$ (1) Å, $V = 3641.0$ (4) Å³, $Z = 8$, $D_x = 1.381$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.54184$ Å, $\mu = 28.865$ cm⁻¹, $F(000) = 1600$, $T = 223$ K, final R (on F) = 0.055 for 1669 observations with $I \geq 3\sigma(I)$. Gly-D,L-Met exists as a cation with the N- and C-termini protonated, the *p*-toluenesulfonate being the counterion. The peptide backbone conformation is a *trans* right-handed helical structure with $\psi_1 = 172.8$ (4), $\omega_1 = -178.9$ (4), $\varphi_2 = -80.6$ (7) and $\psi_2 = -33.8$ (8)°. The methionine residue adopts the

$g^-(tg^-)$ conformation. L-His-L-Leu, (III), $C_{12}H_{20}N_4O_3$, $M_r = 268.32$, crystallizes from aqueous ethanol in the monoclinic space group $P2_1$. $a = 6.559$ (1), $b = 5.451$ (1), $c = 20.463$ (2) Å, $\beta = 99.00$ (1)°, $V = 722.7$ (3) Å³, $Z = 2$, $D_x = 1.233$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.54184$ Å, $\mu = 7.102$ cm⁻¹, $F(000) = 288$, $T = 295$ K, final R (on F) = 0.033 for 1237 observations with $I \geq 3\sigma(I)$. (III) crystallizes as a zwitterion with the N-terminus protonated and the C-terminus ionized. The peptide backbone extends to the C-terminus, which then coils in a helical conformation. Principal torsion angles are $\psi_1 = 164.5$ (2), $\omega_1 = 174.8$ (2), $\varphi_2 = -77.9$ (3) and $\psi_2 = -18.7$ (3)°. The histidyl side chain adopts a *gauche* orientation with the ring twisted slightly from a perpendicular orientation. The leucine residue adopts the $g^-(tg^-)$ conformation. Two intramolecular hydrogen-bonding interactions are proposed, one from the imidazole ring to the ionized C-terminus and the other from the protonated N-terminus to the peptide carbonyl O atom.

Introduction

The positions of amino acids in a peptide sequence and their side-chain bulk and hydrogen-bonding characteristics are factors believed to influence the folding patterns of proteins (Padmanabhan, Marqusee, Ridgeway, Laue & Baldwin, 1990). Conformational studies using crystallographic and