

Table 3. Bond distances (Å) and angles (°)

| | K ₂ SrCu(NO ₂) ₆ | K ₂ SrNi(NO ₂) ₆ |
|----------------|--|--|
| Cu(Ni)—N(1) | 2.310 (2) | 2.078 (1) |
| Cu—N(2) | 2.041 (2) | — |
| Cu—N(3) | 2.029 (2) | — |
| N(1)—O(1) | 1.251 (1) | 1.248 (1) |
| N(2)—O(2) | 1.242 (1) | — |
| N(3)—O(3) | 1.246 (1) | — |
| Sr—O(1) | 2.709 (1) | 2.732 (1) |
| Sr—O(2) | 2.753 (1) | — |
| Sr—O(3) | 2.745 (1) | — |
| K—O(1) | 3.046 (1) | 3.060 (1) |
| K—O(2) | 3.143 (1) | — |
| K—O(3) | 3.106 (1) | — |
| O(1)—N(1)—O(1) | 115.8 (1) | 116.4 (1) |
| O(2)—N(2)—O(2) | 117.1 (1) | — |
| O(3)—N(3)—O(3) | 116.7 (1) | — |

in K₂SrNi(NO₂)₆. No evidence of the NO₂ disorder noted in K₂BaNi(NO₂)₆ crystals is found in the present case. We have observed (Takagi *et al.*, 1975*d*) that the disorder was present in the M₂M'Ni(NO₂)₆ crystals with the large M' counter ion (Ba²⁺, radius 1.35 Å) and was absent in crystals with the smaller ion (Pb²⁺, radius 1.21 Å). The present case (Sr²⁺, radius 1.13 Å) supports our earlier conjecture that ion size rather than bonding properties (Pb²⁺ *vs* Ba²⁺) is the determining factor in allowing or preventing NO₂ group disorder.

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2-(Isopropylideneaminoxy)propion-*p*-bromoanilide

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Abstract. C₁₂H₁₅N₂O₂Br, monoclinic, *P*2₁, *a* = 12.979 (5), *b* = 10.411 (6), *c* = 10.138 (4) Å, β = 96.95 (4)°, *M* = 299.2, *Z* = 4, *D*_x = 1.46 g cm⁻³. The unit cell contains two independent molecules which do not differ significantly in their geometrical parameters; both exhibit the *S* configuration. By chemical correlation this configuration is thereby also confirmed for 2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)propionic acid (TAPA), a valuable reagent for the resolution of racemic Lewis bases.

Introduction. Cell dimensions were determined by a least-squares fit to the settings for 15 reflexions (±*hkl*) on a Syntex *P*2₁ four-circle diffractometer (Mo *K*α, 0.71069 Å). Intensities from a prismatic crystal, 0.18 × 0.22 × 0.42 mm, were collected on the diffractometer with graphite-monochromated Mo *K*α radiation. Measurements were carried out in the θ–2θ mode (3.0 ≤ 2θ ≤ 50.0°) at scan speeds varying linearly between 2.93° min⁻¹ (150 c.p.s. and below) and 29.3° min⁻¹ (5000 c.p.s. and above). Scan and background

times were equal. Three standard reflexions, monitored at regular intervals, did not display any significant variations. Lorentz, polarization and absorption corrections were applied [$\mu(\text{Mo } K\alpha) = 29.3 \text{ cm}^{-1}$]. After application of the rejection criterion $I \geq 2.0\sigma(I)$, where $\sigma(I)$ is based on counting statistics, 3240 unique re-

flexions (one half of the reciprocal sphere) were retained for use in the structure analysis.

The structure was solved by Patterson and Fourier methods. Refinement with anisotropic temperature factors for all the non-hydrogen atoms, with the exception of C(8), was by blocked full-matrix least squares, $\sum w\Delta^2$ being minimized. For each independent molecule, the four benzene H atoms and that at the asymmetric centre were allowed to ride on their bonded C atoms [$r(\text{C-H}) = 1.08 \text{ \AA}$], whereas that at N was allowed to refine freely. A final difference synthesis failed to reveal the positions of the methyl H atoms. The terminal value of $R_G = [\sum w\Delta^2 / \sum wF_o^2]^{1/2}$ was 0.063, with $R_w = \sum w^{1/2}\Delta / \sum w^{1/2}F_o = 0.066$ and $R = 0.083$. Group isotropic temperature factors for the benzene and nonbenzene H atoms refined to 0.068 (13) and 0.036 (16) \AA^2 respectively. The weights were $w = k/[\sigma^2(F_o) + gF_o^2]$ where k and g refined to 1.5546 and 0.002529. With inverse positional coordinates, which correspond to an R form for the molecule, the values of R and R_G deteriorate to 0.081 and 0.107. The S configuration is thereby unequivocally proven. Complex neutral atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed. The atom coordinates and temperature factors are listed in Table 1. The full

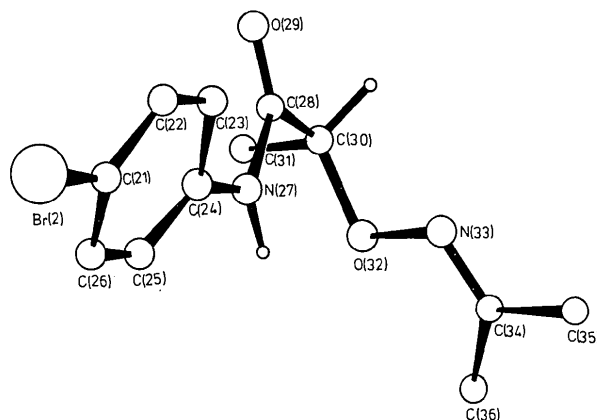


Fig. 1. Molecule 2 in perspective together with the atom-numbering system. An analogous labelling system is used for molecule 1 starting at C(1) instead of C(21).

Table 1. Atom positional parameters ($\times 10^4$) and anisotropic temperature factors ($\text{\AA}^2 \times 10^3$)

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)].$$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₂₃ | <i>U</i> ₁₃ | <i>U</i> ₁₂ |
|-------|-----------|-----------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Br(1) | 9626 (1) | -1556 (1) | 2231 (1) | 104 (1) | 59 (1) | 107 (1) | 15 (1) | 17 (1) | 29 (1) |
| C(1) | 8988 (6) | 101 (9) | 2118 (9) | 48 (4) | 42 (4) | 66 (6) | 0 (5) | 6 (4) | 4 (5) |
| C(2) | 9154 (7) | 873 (9) | 1115 (9) | 57 (6) | 52 (5) | 52 (5) | -6 (5) | 1 (4) | 3 (4) |
| C(3) | 8684 (7) | 2108 (8) | 979 (7) | 67 (6) | 40 (5) | 29 (4) | -2 (4) | 0 (4) | 0 (4) |
| C(4) | 8038 (6) | 2465 (8) | 1956 (8) | 44 (5) | 43 (5) | 40 (5) | -11 (4) | -7 (4) | -6 (4) |
| C(5) | 7902 (7) | 1652 (9) | 3004 (8) | 53 (6) | 56 (5) | 45 (5) | 21 (4) | 11 (4) | 2 (4) |
| C(6) | 8420 (7) | 471 (10) | 3070 (10) | 68 (6) | 66 (6) | 59 (6) | 17 (5) | 2 (5) | 10 (5) |
| N(7) | 7539 (6) | 3666 (8) | 1796 (8) | 63 (5) | 54 (5) | 41 (4) | -6 (4) | 12 (4) | 1 (4) |
| C(8) | 7321 (6) | 4480 (8) | 2758 (8) | 40 (2)† | | | | | |
| O(9) | 7460 (5) | 4246 (6) | 3897 (5) | 82 (4) | 67 (4) | 22 (3) | -3 (3) | 2 (3) | 6 (3) |
| C(10) | 6906 (7) | 5786 (8) | 2261 (7) | 61 (6) | 48 (5) | 38 (5) | -13 (4) | -12 (4) | 3 (4) |
| C(11) | 6378 (10) | 6509 (12) | 3277 (11) | 104 (9) | 75 (8) | 88 (8) | -19 (6) | -3 (7) | 35 (7) |
| O(12) | 6299 (5) | 5773 (6) | 1009 (6) | 64 (4) | 52 (4) | 63 (4) | 5 (3) | 5 (3) | 6 (3) |
| N(13) | 5380 (5) | 5016 (8) | 1165 (7) | 61 (4) | 56 (4) | 59 (5) | 4 (4) | -7 (4) | 6 (5) |
| C(14) | 4724 (7) | 5103 (9) | 129 (9) | 71 (6) | 58 (6) | 48 (5) | 10 (5) | -2 (5) | 9 (6) |
| C(15) | 3706 (9) | 4361 (12) | 159 (12) | 79 (8) | 88 (8) | 109 (9) | 19 (7) | -26 (7) | -14 (7) |
| C(16) | 4848 (9) | 5855 (13) | -1099 (10) | 86 (8) | 118 (10) | 56 (6) | -4 (7) | -14 (6) | 11 (7) |
| Br(2) | 9907 (1) | 0 | 7212 (1) | 64 (1) | 48 (1) | 135 (1) | 5 (1) | 22 (1) | -6 (1) |
| C(21) | 9160 (5) | 8424 (9) | 7083 (8) | 38 (4) | 48 (5) | 53 (5) | 10 (5) | -3 (4) | -3 (4) |
| C(22) | 8527 (7) | 8108 (8) | 8047 (9) | 64 (6) | 40 (5) | 61 (6) | 5 (4) | 14 (5) | -4 (4) |
| C(23) | 8028 (7) | 6938 (8) | 8002 (9) | 54 (6) | 46 (5) | 65 (6) | 11 (5) | 13 (5) | -1 (4) |
| C(24) | 8108 (6) | 6120 (7) | 6914 (7) | 42 (4) | 40 (5) | 30 (4) | -14 (4) | -7 (4) | 3 (4) |
| C(25) | 8731 (7) | 6491 (10) | 6019 (9) | 47 (6) | 72 (7) | 53 (6) | 1 (5) | 10 (5) | 8 (5) |
| C(26) | 9259 (6) | 7611 (9) | 6075 (8) | 47 (5) | 72 (6) | 42 (5) | 6 (5) | 13 (4) | -6 (5) |
| N(27) | 7562 (5) | 4925 (6) | 6777 (6) | 57 (4) | 42 (4) | 17 (3) | -12 (3) | -6 (3) | -8 (4) |
| C(28) | 7334 (7) | 4193 (8) | 7803 (9) | 57 (6) | 50 (5) | 48 (6) | 10 (5) | -1 (5) | 10 (4) |
| O(29) | 7573 (5) | 4436 (6) | 8976 (6) | 96 (5) | 49 (3) | 34 (3) | 2 (3) | 8 (3) | -1 (3) |
| C(30) | 6800 (8) | 2918 (9) | 7396 (10) | 71 (7) | 61 (6) | 64 (7) | 11 (5) | 1 (5) | -12 (5) |
| C(31) | 7610 (11) | 1834 (10) | 7359 (13) | 115 (11) | 53 (6) | 124 (10) | -6 (7) | -73 (8) | 32 (6) |
| O(32) | 6238 (5) | 2931 (5) | 6065 (5) | 60 (4) | 38 (3) | 45 (3) | -4 (2) | -12 (2) | 4 (3) |
| N(33) | 5367 (5) | 3769 (6) | 6044 (7) | 50 (4) | 40 (4) | 70 (5) | 1 (4) | 3 (4) | 4 (3) |
| C(34) | 4783 (7) | 3661 (7) | 4937 (10) | 50 (5) | 39 (5) | 67 (6) | 22 (4) | -12 (5) | -5 (4) |
| C(35) | 3831 (8) | 4495 (11) | 4799 (11) | 65 (7) | 61 (6) | 115 (9) | 0 (6) | -8 (6) | 17 (5) |
| C(36) | 4949 (8) | 2765 (11) | 3858 (9) | 77 (7) | 87 (8) | 54 (6) | 28 (6) | 0 (5) | 8 (6) |

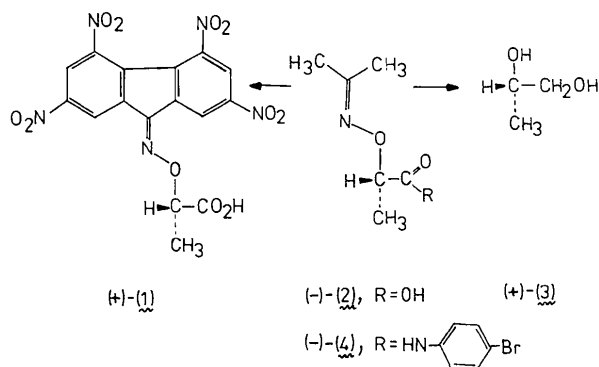
† C(8) was refined isotropically.

Table 2. Bond lengths (Å)

| | | | |
|-------------|------------|-------------|------------|
| C(1)—C(2) | 1.330 (13) | C(2)—C(3) | 1.421 (12) |
| C(3)—C(4) | 1.420 (12) | C(4)—C(5) | 1.386 (12) |
| C(5)—C(6) | 1.397 (13) | C(6)—C(1) | 1.346 (13) |
| Br(1)—C(1) | 1.911 (9) | C(4)—N(7) | 1.407 (11) |
| N(7)—C(8) | 1.347 (11) | C(8)—O(9) | 1.174 (9) |
| C(8)—C(10) | 1.527 (11) | C(10)—C(11) | 1.508 (15) |
| C(10)—O(12) | 1.411 (9) | O(12)—N(13) | 1.452 (10) |
| N(13)—C(14) | 1.271 (11) | C(14)—C(15) | 1.534 (15) |
| C(14)—C(16) | 1.495 (15) | N(7)—H(7) | 0.71 (7) |
| C(21)—C(22) | 1.387 (12) | C(22)—C(23) | 1.380 (12) |
| C(23)—C(24) | 1.407 (11) | C(24)—C(25) | 1.341 (12) |
| C(25)—C(26) | 1.350 (14) | C(26)—C(21) | 1.349 (12) |
| Br(2)—C(21) | 1.902 (9) | C(24)—N(27) | 1.432 (10) |
| N(27)—C(28) | 1.353 (11) | C(28)—O(29) | 1.216 (11) |
| C(28)—C(30) | 1.530 (13) | C(30)—C(31) | 1.545 (16) |
| C(30)—O(32) | 1.453 (11) | O(32)—N(33) | 1.427 (9) |
| N(33)—C(34) | 1.282 (11) | C(34)—C(35) | 1.506 (14) |
| C(34)—C(36) | 1.470 (14) | N(27)—H(27) | 0.92 (6) |

covariance matrix was used in the estimation of standard deviations for the bond lengths presented in Table 2. Fig. 1 shows the atom-numbering.*

Discussion. 2-(2,4,5,7-Tetranitro-9-fluorenylidene)propionic acid (TAPA) (1), which was first employed in the separation of enantiomers of hexahelicene (Newman, Lutz & Lednicer, 1955; Newman & Lednicer, 1956), has since proved to a valuable reagent for the optical resolution of certain aromatic compounds (*e.g.* racemic Lewis bases), especially those which do not have the functional groups usually needed to effect resolution by conventional reagents. A knowledge of the absolute configuration of (1) is essential to an understanding of the interactions in the diastereomeric charge-transfer complex.



(-)-(2) can be converted into (+)-(1) by trans-oximation with 2,4,5,7-tetranitrofluorenone (Newman, Lutz & Lednicer, 1955). Reduction of (2) with LiAlH_4 in ether gives 1,2-propanediol (3), which may be transformed into the dibenzoate to facilitate characteriza-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31790 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

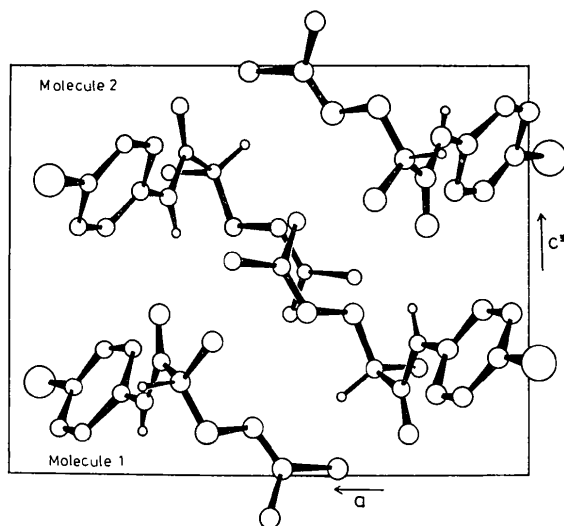


Fig. 2. The projection of the structure perpendicular to [010].

tion. Hydrolysis of (-)-(2) ($[\alpha]_{578}^{22} = -34^\circ$; $C=1$; H_2O) yields *S*-(+)-(3) ($[\alpha]_{578}^{22} = 8.2^\circ$; $C=0.17$; CH_3OH); analogously (+)-(2) leads to (-)-(3) (Kemmer, Sheldrick & Brockmann, 1976). As no attack at the asymmetric centre is involved in this correlation, the *S* configuration is unambiguously established for (+)-TAPA. In order to confirm this finding, an X-ray analysis was carried out on (-)-(4), which is readily accessible from (-)-(2) by aminolysis of the corresponding carboximidazole (Staab, 1962) with *p*-bromoaniline.

The unit cell contains two independent molecules of (4), both in the *S* configuration (Fig. 2), which do not differ significantly in their geometrical parameters. Trigonal coordination is observed at the anilide N(7) and N(27), the sum of their valence angles being 359.5° and 359.7° respectively. The short N(7)—C(8) and N(27)—C(28) distances of 1.347 (11) and 1.353 (11) Å are indicative of a strong interaction between the N lone pair and the C=O and benzene π -systems.

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