

The Crystal and Molecular Structure of 2-Nitro-1,3-indandione Dihydrate. A Hydronium Nitronate

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The crystal structure of 2-nitro-1,3-indandione dihydrate, $C_9H_9O_6N$, has been determined. The crystals belong to the monoclinic space group $P2_1/c$; the cell dimensions are $a = 9.756$ (2), $b = 5.149$ (1), $c = 19.911$ (5) Å, $\beta = 102.49$ (2)°, with $Z = 4$, $D_c = 1.55$, $D_o = 1.58$ g cm⁻³. Refinement by full-matrix least-squares calculations gave an R index of 0.069. The compound crystallizes as a hydronium salt with an asymmetric $H_3O_2^+$ arrangement. The bonding distances indicate that the negative charge of the anion is delocalized over that part of the molecule which contains the O atoms. The description of the electronic structure in the molecule obtained from bond distances is strongly supported by ¹³C NMR spectroscopy.

Introduction

This structure determination is part of a more comprehensive study of the nitro group in three different states: nitro group, acid nitro group and nitronate salt. 2-Nitro-1,3-indandione dihydrate (NIDADO) is reported to be a very strong acid (Wanag, 1936), which crystallizes as a stable hydronium nitronate salt (Stradins, Neilands, Freimanis & Vanags, 1959; Neilands, Stradins & Vanags, 1960). Accordingly, a structure determination was carried out.

Crystal data

Molecular formula $C_9H_9O_6N$, FW 227.18, $F(000) = 472$, m.p. 113–114°C (uncorrected), crystal habit: yellow prism. Monoclinic cell parameters: $a = 9.756$ (2), $b = 5.149$ (1), $c = 19.911$ (5) Å, $\beta = 102.49$ (2)°; $D_o = 1.58$, $D_c = 1.55$ g cm⁻³. Systematic absences $h0l: l = 2n + 1, 0k0: k = 2n + 1$; space group $P2_1/c$, $Z = 4$, $V = 976.5$ Å³, $\mu(\text{Mo } K\alpha) = 1.70$ cm⁻¹.

Experimental

Commercially available 2-nitro-1,3-indandione was recrystallized from hot water and the crystals obtained were used.

Accurate unit-cell dimensions were determined by a least-squares refinement of data measured from a Guinier powder photograph taken with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and calibrated with quartz as an internal standard.

The three-dimensional X-ray data were obtained using a three-circle Enraf–Nonius diffractometer and Zr-filtered Mo $K\alpha$ radiation. A reflexion was designated unobserved if $I \leq 2.2\sigma(I)$. The single reflexion 0,0,12 was monitored every 10 reflexions. Lorentz and

polarization corrections were applied, but no extinction or absorption corrections were made. X-ray measurement data are given in Table 1.

All calculations were performed on an IBM 370/165 computer using the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The structure was solved by direct methods using the XRAY system subprograms *NORMSF*, *SINGEN* and *PHASE*. 141 phases were determined in this way. An E map computed with these 141 phases revealed all the non-hydrogen atoms. The succeeding structure factor calculation, using the atomic parameters from the E map and all the observed data, gave an initial residual ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.39. The structural parameters were refined by full-matrix least squares. The residual R was 0.091 when the refinement stopped (anisotropic temperature factors, nonhydrogen atoms).

A subsequent difference synthesis was calculated with restricted data ($\sin \theta / \lambda < 0.4$ Å⁻¹). This calculation revealed the positions of all the H atoms. The

Table 1. X-ray measurement data for 2-nitro-1,3-indandione dihydrate

| | |
|--|---|
| Radiation | Mo $K\alpha$ ($\lambda = 0.7107$ Å) |
| Filter | Zr |
| Crystal size (approximate) | 0.4 × 0.5 × 0.6 mm |
| Crystal mounting | Parallel to a |
| X-ray detection | Scintillation detector with pulse-height analyser |
| Collection method | ω scan |
| 2 ω scan range | 1.6° |
| 2 ω scan speed | 0.6° min ⁻¹ |
| Background: time of stationary count at beginning and end of each scan | 80 s |
| 2 θ maximum | 30° |
| Number of unique data measured | 2613 |
| Number of observed data | 1703 |

positional H parameters were refined separately ($\sin \theta/\lambda < 0.4 \text{ \AA}^{-1}$). The H atoms were given the same isotropic temperature factors as the atoms to which they are bonded. The quantity minimized in the final refinement cycles was $\sum w(|F_o| - |F_c|)^2$ and weights were calculated from Cruickshank's (1965) weighting scheme. Unobserved data were not included in the calculations. The final R was 0.069. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates are given in Table 2.* Bond distances and angles are given in Figs. 1 and 2.

The ^{13}C NMR spectra were recorded on a Jeol FX60 Fourier Transform spectrometer operating at 15.03 MHz using a deuterium internal lock. The proton decoupled spectrum was obtained using noise decoupling and 8 K data points. Undecoupled spectra were recorded in the gated decoupling mode with repetition times equal to twice the acquisition time. In all cases the pulse angles were equal to 60° .

^{13}C chemical shifts relative to TMS of NIDADO are given in Table 4. The sample used was a 10% solution of NIDADO in D_2O with CH_3OH as a secondary reference. The assignments of the lines have been based

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32625 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Final atomic coordinates with standard deviations ($\times 10^4$, for H $\times 10^3$)

| | x | y | z |
|-------|----------|-----------|----------|
| O(1) | 4733 (3) | 9423 (6) | 3630 (2) |
| O(3) | 753 (3) | 3077 (7) | 4338 (2) |
| O(4) | 3927 (4) | 7199 (6) | 4789 (2) |
| O(5) | 2110 (4) | 8873 (7) | 5117 (2) |
| O(6) | 6279 (4) | 5550 (7) | 4106 (2) |
| O(7) | 8772 (4) | 6870 (7) | 4154 (2) |
| N(2) | 2944 (4) | 8880 (6) | 4716 (2) |
| C(1) | 3694 (4) | 735 (7) | 3682 (2) |
| C(2) | 2814 (4) | 635 (7) | 4187 (2) |
| C(3) | 1715 (4) | 2626 (7) | 4035 (2) |
| C(3a) | 1970 (4) | 4010 (7) | 3409 (2) |
| C(4) | 1244 (4) | 6085 (8) | 3044 (2) |
| C(5) | 1679 (5) | 6914 (9) | 2446 (2) |
| C(6) | 2788 (5) | 5706 (9) | 2222 (2) |
| C(7) | 3545 (5) | 3651 (9) | 2607 (2) |
| C(7a) | 3096 (4) | 2831 (7) | 3190 (2) |
| H(4) | 47. (6) | 708. (11) | 323. (2) |
| H(5) | 128. (6) | 849. (12) | 218. (2) |
| H(6) | 323. (6) | 622. (12) | 181. (2) |
| H(7) | 434. (6) | 280. (10) | 241. (2) |
| H(61) | 556. (6) | 707. (12) | 396. (3) |
| H(64) | 625. (6) | 423. (13) | 447. (3) |
| H(67) | 753. (6) | 588. (12) | 415. (3) |
| H(73) | 939. (6) | 530. (12) | 420. (3) |
| H(75) | 899. (6) | 793. (12) | 458. (3) |

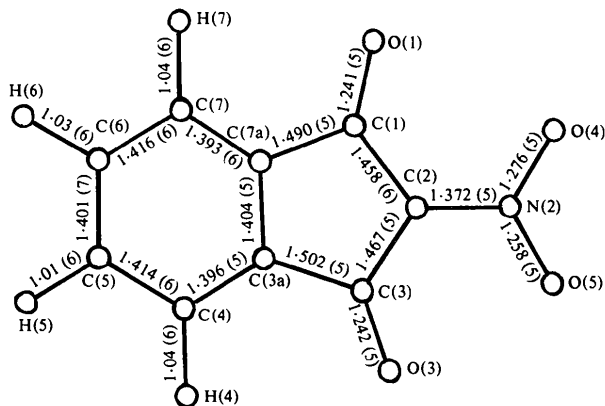


Fig. 1. Bond distances (\AA) and atom-numbering scheme for the 1,3-indandione-2-nitronate ion. Estimated standard deviations are given in parentheses.

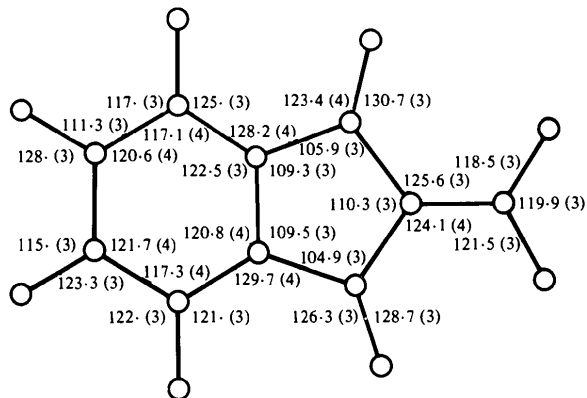


Fig. 2. Angles ($^\circ$) in the 1,3-indandione-2-nitronate ion. Estimated standard deviations in parentheses.

upon the undecoupled spectrum and the well known substituent effects in aromatic compounds (Stothers, 1972).

Discussion

The distance C(2)—N(2) (1.372 \AA) is in agreement with the C—N bond lengths found in nitronates: bis(propene-2-nitronato)copper(II), 1.35 \AA (Simonsen, 1973); dirubidium 1,1,2,2-tetranitroethanediide, 1.378 and 1.381 \AA (Klewe, 1972); dipotassium nitroacetate, 1.39 \AA (Sutor, Llewellyn & Maslen, 1954). The distance O(6)—O(7), 2.507 \AA , compares well with the corresponding distance found in hydronium salts: hydronium nitranilate, 2.440 \AA (Andersen & Andersen, 1975); hydronium cyananilate, 2.441 \AA (Andersen & Andersen, 1975); picrylsulphonic acid tetrahydrate, 2.436 \AA (Lundgren & Tellgren, 1974). Hence, the nitroindandione dihydrate is considered to be a

Table 3. Bond lengths (Å) in 2-nitro-1,3-indandione dihydrate compared with corresponding bonds in four other 1,3-indandione systems

The numbering of the atoms refers to Fig. 1.

NIDADO: 2-nitro-1,3-indandione dihydrate

DICYM: 2-dicyanomethyleneindan-1,3-dione (Silverman, Krukoniš & Yannoni, 1974).

PHENY: 2-phenyl-1,3-indandione (Bravic, Gaultier & Hauw, 1974a)

ETPHE: 2-ethyl-2-phenyl-1,3-indandione (Bravic, Gaultier & Hauw, 1974b)

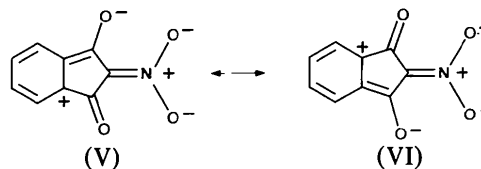
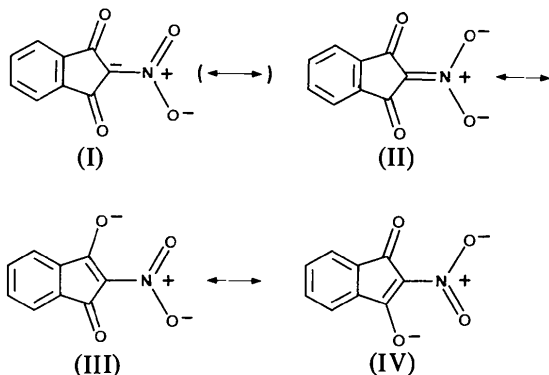
IDADO: 1,3-indandione (Bravic, Bechtel, Gaultier & Hauw, 1976)

| | NIDADO | DICYM | PHENY | ETPHE | IDADO |
|-------------|--------|-------|-------|-------|-------|
| C(1)–C(2) | 1.458 | 1.505 | 1.514 | 1.546 | 1.508 |
| C(2)–C(3) | 1.467 | 1.500 | 1.540 | 1.542 | 1.516 |
| C(3)–C(3a) | 1.502 | 1.481 | 1.489 | 1.484 | 1.476 |
| C(3a)–C(7a) | 1.404 | 1.402 | 1.397 | 1.388 | 1.387 |
| C(3a)–C(4) | 1.396 | 1.385 | 1.376 | 1.389 | 1.387 |
| C(4)–C(5) | 1.414 | 1.376 | 1.384 | 1.382 | 1.378 |
| C(5)–C(6) | 1.401 | 1.393 | 1.412 | 1.396 | 1.379 |
| C(6)–C(7) | 1.416 | 1.380 | 1.351 | 1.377 | 1.376 |
| C(7)–C(7a) | 1.393 | 1.392 | 1.399 | 1.391 | 1.380 |
| C(7a)–C(1) | 1.490 | 1.475 | 1.464 | 1.479 | 1.477 |
| C(1)–O(1) | 1.241 | 1.212 | 1.210 | 1.211 | 1.215 |
| C(3)–O(3) | 1.242 | 1.208 | 1.212 | 1.211 | 1.211 |

hydronium nitronate. An earlier spectroscopic investigation gave the same result (Stradins, Neiland, Freimanis & Vanags, 1959).

The crystal structures of some related indandiones have been reported previously (Table 3). Comparison of NIDADO with these compounds reveals several differences: shortenings are seen for the bonds C(1)–C(2) and C(2)–C(3) whereas O(1)–C(1), O(3)–C(3), C(1)–C(7a), C(3)–C(3a), C(4)–C(5) and C(6)–C(7) are elongated.

A delocalization of the negative charge, indicated by the resonance formulae II–IV, can explain the observed differences in the bond distances of the system O(1), C(1), C(2), C(3), O(3) [N(2), O(4), O(5)]. The elongated bonds C(1)–C(7a) and C(3)–C(3a) comply with a smaller contribution from the mesomeric forms V and VI when NIDADO is compared with DICYM, PHENY, ETPHE and IDADO. The compounds PHENY, ETPHE and IDADO have sp^3 -hybridized C(2), whereas this atom in NIDADO and DICYM is sp^2 hybridized.



The values of the ^{13}C chemical shifts of NIDADO are remarkable with regard to the low value for the carbonyl carbon. Compared with other ketones, this C atom is shifted about 15 ppm upfield. This indicates an unusually high electron density at C(1) and C(3), which could be explained as being due to a high delocalization of the excess charge in accordance with the resonance structures III and IV.

The effect of this delocalization is also seen to influence the chemical shift of the benzenoid C atoms. Nelson, Levy & Cargioli (1972) have established a correlation between ^{13}C chemical shift of disubstituted benzenes and the total charge density on C calculated in the CNDO/2 approximation. In Table 4 the total charge densities of some of the C atoms in NIDADO estimated from this correlation have been given. Since the total charge density on the C atoms in benzene itself in these calculations is claimed to be +0.02 e, it can be concluded that C(3a) and C(5) in NIDADO have a slightly positive charge, while C(4) has a negative charge compared with benzene. The effect of charge delocalization in NIDADO is strongly supported by the relatively high value for the chemical shift of C(2), just in the range acceptable for double-bonded C atoms. This shows that resonance structure I makes a relatively unimportant contribution to the description of the electronic structure in NIDADO. Thus, the important mesomers of NIDADO seem to be (II), (III) and (IV).

The nitronate exhibits minor deviations from planarity (Table 5). The carbonyl groups have a twisted conformation relative to the benzene ring, which makes an angle of 4.85° with the plane O(4)—N(2)—O(5).

Table 4. ^{13}C chemical shift (δ) in 2-nitro-1,3-indandione

| Atom (<i>i</i>) | $\delta(i)$ (ppm)* | Total charge density† |
|-------------------|--------------------|-----------------------|
| C(1) | 184.97 | |
| C(2) | 120.91 | |
| C(3a) | 135.15 | +0.06 |
| C(4) | 121.04 | -0.03 |
| C(5) | 133.52 | +0.04 |

* Uncertainty: ± 0.07 ppm.

† Estimated from Nelson *et al.* (1972).

Table 5. Distances of atoms (\AA) from the least-squares plane

The plane is in the form $0.52854x + 0.64789y + 0.54862z = 8.55511$. The coordinates *x*, *y* and *z* are expressed parallel to the orthogonal axial directions **a**, **b**, and **c***

| | | | | | |
|-------|--------|-------|--------|-------|--------|
| C(1)† | 0.019 | C(6) | -0.014 | O(4)† | -0.113 |
| C(2)† | -0.045 | C(7) | 0.013 | O(5)† | -0.216 |
| C(3)† | -0.075 | C(7a) | -0.003 | H(4)† | 0.10 |
| C(3a) | -0.006 | N(2)† | -0.200 | H(5)† | 0.10 |
| C(4) | 0.005 | O(1)† | 0.074 | H(6)† | 0.04 |
| C(5) | 0.005 | O(3)† | -0.166 | H(7)† | -0.02 |

† These atoms were not included in the calculation of the least-squares plane.

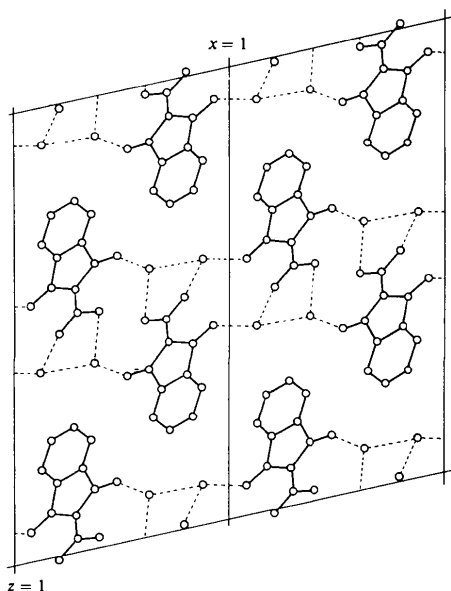


Fig. 3. Packing view of the crystal structure (*b*-axis projection). The dotted lines represent the hydrogen-bonding system.

Fig. 3 shows a projection of the crystal structure along the *y* axis. The nitroindandione molecules are connected by hydrogen bonds. The carbonyl O atoms, as well as the nitro O atoms, are acceptors in hydrogen bonds from the H_3O_2^+ arrangement.

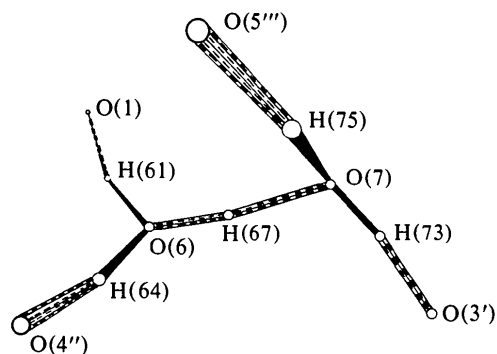


Fig. 4. Perspective drawing of the hydrogen-bonding system in 2-nitro-1,3-indandione dihydrate. The *y* coordinates associated with the O atoms in this drawing are: O(1) 0.9423, O(3') 0.3077, O(4'') 0.2801, O(5''') 1.1127, O(6) 0.5550, and O(7) 0.6870.

Table 6. Distances (\AA) and bond angles ($^\circ$) associated with the hydrogen-bonding system

Estimated standard deviations are given in parentheses.

| | | | |
|------------|-----------|------------------|-----------|
| O(1)—O(6) | 2.556 (4) | O(1)—O(6)—O(4) | 125.3 (2) |
| O(1)—H(61) | 1.52 (6) | O(1)—O(6)—O(7) | 107.0 (2) |
| O(3)—O(7) | 2.716 (5) | O(4)—O(6)—O(7) | 111.0 (1) |
| O(3)—H(73) | 1.73 (6) | H(61)—O(6)—H(64) | 125 (5) |
| O(4)—O(6) | 2.660 (5) | H(61)—O(6)—H(67) | 121 (4) |
| O(4)—H(64) | 1.69 (6) | H(64)—O(6)—H(67) | 103 (4) |
| O(5)—O(7) | 2.863 (5) | O(3)—O(7)—O(5) | 139.9 (2) |
| O(5)—H(75) | 2.13 (6) | O(3)—O(7)—O(6) | 117.8 (2) |
| O(6)—O(7) | 2.507 (5) | O(5)—O(7)—O(6) | 80.3 (1) |
| O(6)—H(61) | 1.05 (6) | H(67)—O(7)—H(73) | 103 (4) |
| O(6)—H(64) | 1.00 (6) | H(67)—O(7)—H(75) | 104 (5) |
| O(6)—H(67) | 1.21 (6) | H(73)—O(7)—H(75) | 110 (5) |
| O(7)—H(67) | 1.32 (6) | O(1)—H(61)—O(6) | 166 (6) |
| O(7)—H(73) | 1.00 (6) | O(4)—H(64)—O(6) | 163 (6) |
| O(7)—H(75) | 0.99 (6) | O(6)—H(67)—O(7) | 165 (5) |
| | | O(3)—H(73)—O(7) | 167 (5) |
| | | O(5)—H(75)—O(7) | 130 (4) |

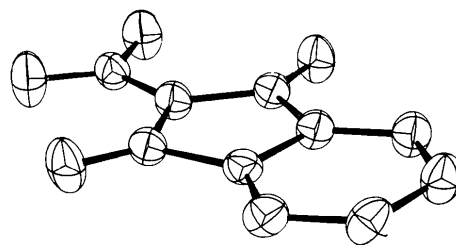


Fig. 5. Perspective drawing of the 1,3-indandione-2-nitronate ion. Atoms are represented by ellipsoids enclosing 50% of the thermal displacements.

O(6) in the H_5O_2^+ unit is associated with shorter O—O interactions than is O(7) (Fig. 4, Table 6). As pointed out by Andersen (1971) this feature could be taken as evidence that the H_5O_2^+ ion is preferably described by the formula $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$. The present investigation confirms this conclusion (Table 6). A neutron diffraction investigation (Lundgren & Tellgren, 1974) has shown the existence of the hydrated H_3O^+ ion in picrylsulphonic acid tetrahydrate.

A perspective drawing of the 1,3-indandione-2-nitronate ion is shown in Fig. 5.

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The Crystal and Molecular Structure of Episparteine N(16)-Oxide Sesquiperchlorate

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$[(\text{C}_{15}\text{H}_{27}\text{N}_2\text{O})_2\text{H}]^{3+}(\text{ClO}_4^-)_3$; $M_r = 802.1$; monoclinic, $C2$; $a = 25.943(3)$, $b = 8.137(1)$, $c = 9.132(1)$ Å; $\beta = 105.13(1)^\circ$; $Z = 2$; $D_m = 1.431$, $D_x = 1.440$ g cm $^{-3}$; $R = 0.035$ and $R_w = 0.030$ for 1138 reflections. The boat conformation for ring C deduced from NMR data is observed. The perchlorate group is disordered around the twofold axis. The O atom in the N-oxide group forms a strong hydrogen bond with the equivalent O atom of another molecule [O...O distance equals 2.435(4) Å].

Introduction

The structure of sparteine N(16)-oxide sesquiperchlorate was determined by Srivastava & Przybylska (1969) using X-ray analysis. The sparteine skeleton of this compound (Fig. 1a) consists of a two-chair *trans*-quinolizidine A/B system, and a two-chair *cis*-quinolizidine C/D system.

Episparteine N(16)-oxide, the compound for the present study, was obtained by Bratek-Wiewiórowska, Skolik, Łangowska & Wiewiórowski (1974) as a product of a mild reduction of the lactam group of

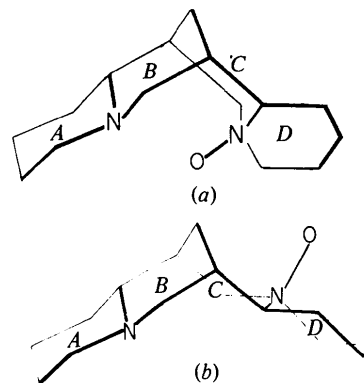


Fig. 1. (a) Sparteine N(16)-oxide. (b) Episparteine N(16)-oxide.

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