The Action of Nitrogen Dioxide and Nitric Oxide on Humulene, $C_{15}H_{24}$. *X*-Ray Crystallographic Determination of the Stereochemistries and Conformations of Humulene Nitrosite, Dinitrohumulene, and Nitronitratohumulene

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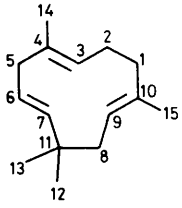
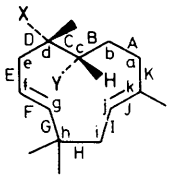
The stereochemistries and conformations of humulene nitrosite (2), dinitrohumulene (3), and nitronitratohumulene (4) have been determined by *X*-ray analyses of their crystal structures. The compounds are shown to result from *cis* addition to humulene (1). The common ring conformation in compounds (2), (3), and (4) differs from that in humulene. A spread of C–C–C angles in the eleven-membered rings indicates steric strain and these results are reproduced in force-field calculations on the hexamethylcycloundecadiene (5). Crystallographic data are: humulene nitrosite, a = 6.484(2), b = 18.139(8), c = 14.294(3) Å, β = 101.33(2)°, Z = 4, space group $P2_1/n$; dinitrohumulene, a = 6.422(2), b = 18.177(2), c = 14.218(2) Å, β = 100.69(2)°, Z = 4, space group $P2_1/n$; nitronitratohumulene, a = 7.665(2), b = 11.908(2), c = 18.170(4) Å, Z = 4, space group $Pc2_1n$. *X*-Ray intensity measurements were made on an automatic four-circle diffractometer and least-squares adjustment of the atomic co-ordinates and thermal parameters converged at R 0.071 for compound (2), 0.042 for compound (3), and 0.052 for compound (4).

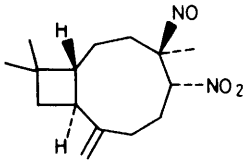
HUMULENE (1) reacts with nitrogen dioxide and nitric oxide to give humulene nitrosite (2), dinitrohumulene (3), and nitronitratohumulene (4).[1] We undertook *X*-ray analyses to define the stereochemistries and conformations of compounds (2), (3), and (4). The *X*-ray intensities were measured on an automatic diffractometer and the atomic parameters obtained by direct phasing procedures and least-squares calculations. The derived molecular structures are shown in Figures 1—3, and the



(1)



(2) X = NO, Y = NO_2
(3) X = NO_2, Y = NO_2
(4) X = ONO_2, Y = NO_2
(5) X = Me, Y = Me



(6)

torsion angles describing the ring conformations are listed in Table 1. Our results establish the stereochemistries shown in structures (2)—(4) and indicate that these compounds are formed by *cis* addition to a double bond of humulene. The stereospecificity of the addition to humulene is identical with that involved in the formation of caryophyllene nitrosite (6).[2] On the other hand, the reaction of nitrogen dioxide radicals with simpler cyclic olefins frequently lacks stereospecificity, and then *trans* addition predominates.[3]

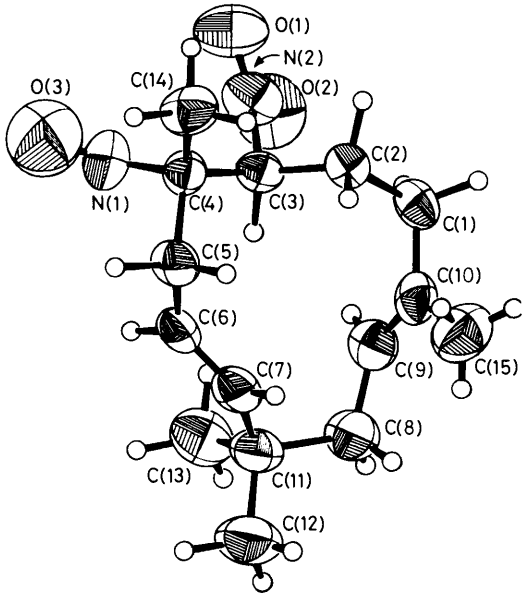


FIGURE 1 The molecular structure of humulene nitrosite (2). The thermal ellipsoids of the C, N, and O atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0.1 Å. The numbering system for the C atoms is based on that commonly used for germacranolide sesquiterpenes

Compounds (2)—(4) exhibit a common ring conformation which differs in the region of the NO, NO_2, and ONO_2 substituents from the conformation of humulene (see Table 1); the *trans* double bond in humulene that is involved in the addition reaction has a torsion angle of 162° whereas the corresponding (reduced) bond in compounds (2)—(4) has a torsion angle of *ca.* −80°. Anet and Rawdah have discussed the conformational proper-

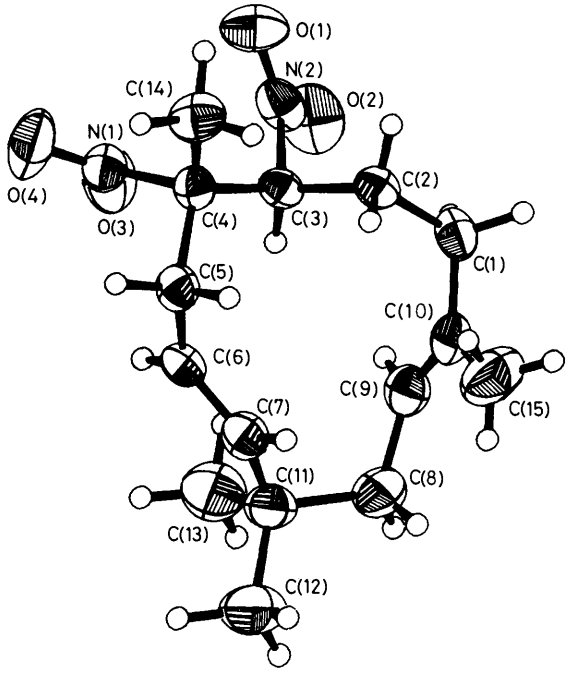


FIGURE 2 The molecular structure of dinitrohumulene (3). Thermal ellipsoids as in Figure 1

ties of cycloundecane and have derived six low-energy conformations by force-field calculations [4] but none of the conformations corresponds to the conformation found in compounds (2)—(4). A full understanding of

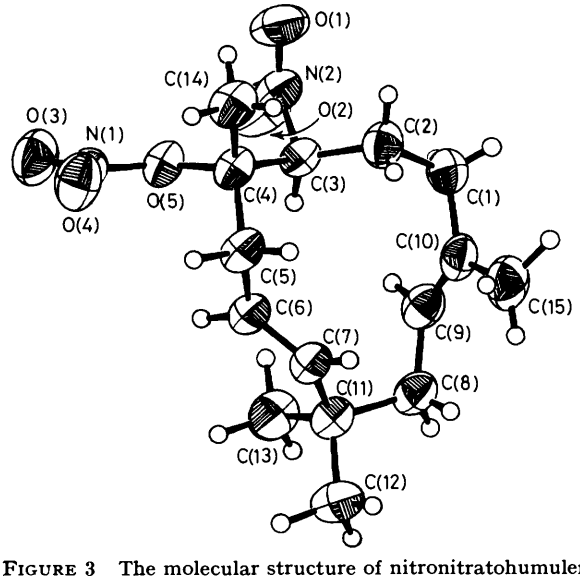


FIGURE 3 The molecular structure of nitronitratohumulene (4). Thermal ellipsoids as in Figure 1

the conformational properties of substituted eleven-membered rings undoubtedly requires further *X*-ray studies and force-field calculations.

The bond angles in the eleven-membered ring in compounds (2)—(4) exhibit a spread of values, indicating some degree of steric strain. Thus, the C–C=C angles range from 121.5 to 129.3°, with the C–C(C)=C angle k smaller than the C–C(H)=C angles f, g, and j. The C–C(sp^3)–C angles range from 105.8 to 116.5°, with angle h smallest (105.8—107.1°) and angle c largest (114.9—116.5°). Force-field calculations for the hydrocarbon analogue (5) in the conformation of compounds (2)—(4) reproduce these characteristic features of the ring (see Table 2). The *trans* double bonds in compounds (2)—(4), moreover, have torsion angles that differ notably from the ideal value of 180° and these departures from planarity are also reproduced by the force-field calculations (Table 1). These calculations were performed with the hydrocarbon force field developed by White and Bovill [5] with a full-matrix procedure for energy minimization.[6]

TABLE 1

Conformational comparisons

C–C–C–C Ring torsion angles (°) in the eleven-membered rings of humulene–2AgNO$_3$ (1),[a] humulene nitrosite (2), dinitrohumulene (3), and nitronitratohumulene (4) are from *X*-ray studies. Torsion angles for the hexamethylcycloundecadiene (5) are from force-field calculations

Torsion angle about bond	(1)	(2)	(3)	(4)	(5)
A	−35	−78	−80	−82	−84
B	−77	154	152	154	147
C	162	−80	−79	−75	−67
D	−95	−47	−45	−48	−48
E	94	119	120	123	130
F	−156	−168	−167	−167	−169
G	102	120	119	117	110
H	−55	−45	−45	−45	−42
I	126	104	104	101	101
J	−172	−166	−167	−166	−169
K	109	95	97	98	95

[a] A. T. McPhail and G. A. Sim, *J. Chem. Soc. B*, 1966, 112.

TABLE 2

Comparison of bond angles (°) in compounds (2), (3), and (4) with force-field results for compound (5)

Bond angle	(2)	(3)	(4)	(5)
a	110.8	110.2	109.1	111.2
b	112.7	112.8	112.0	114.0
c	116.5	114.9	115.0	114.6
d	109.0	109.7	109.2	112.1
e	114.0	114.8	113.4	113.2
f	123.3	124.3	123.2	123.2
g	127.8	129.3	127.6	125.1
h	105.8	106.3	107.1	108.3
i	112.7	112.7	113.4	111.7
j	127.2	126.8	126.3	125.8
k	121.7	121.7	121.5	120.4

EXPERIMENTAL

Crystal Data.—Humulene nitrosite (2), $C_{15}H_{24}N_2O_3$, M = 280.39, Monoclinic, space group $P2_1/n$, a = 6.484(2), b = 18.139(8), c = 14.294(3) Å, β = 101.33(2)°, U = 1 648 Å^3, D_c = 1.130 g cm^{-3}, Z = 4, $F(000)$ = 608, μ(Mo-K_α) = 0.85 cm^{-1} (crystal form: needle).

Dinitrohumulene (3), $C_{15}H_{24}N_2O_4$, M = 296.39, Monoclinic, space group $P2_1/n$, a = 6.422(2), b = 18.177(2), c = 14.218(2) Å, β = 100.69(2)°, U = 1 631 Å^3, D_c = 1.207 g cm^{-3}, Z = 4, $F(000)$ = 640, μ(Mo-K_α) = 0.94 cm^{-1}.

Nitronitratohumulene (4), $C_{15}H_{24}N_2O_5$, M = 312.40,

Orthorhombic, space group $Pc2_1n$, $a = 7.665(2)$, $b = 11.908(2)$, $c = 18.170(4)$ Å, $U = 1\,658$ Å^3, $D_c = 1.251$ g cm^{-3}, $Z = 4$, $F(000) = 672$, μ(Cu-K_α) = 7.88 cm^{-1}.

Crystallographic Measurements.—Cell dimensions for each compound were derived from least-squares treatment of the setting angles for 25 reflections measured on an Enraf-Nonius CAD4 diffractometer. Mo-K_α Radiation was employed for humulene nitrosite and dinitrohumulene and Cu-K_α radiation for nitronitratohumulene. For intensity measurements, reflections were surveyed by θ–ω scans in the ranges $\theta \leqslant 27°$ (humulene nitrosite and dinitrohumulene), $\theta \leqslant 72°$ (nitronitratohumulene). Application of the criterion $I > 2.5\sigma(I)$ gave 1 221 reflections for humulene nitrosite, 1 617 for dinitrohumulene, and 1 610 for nitronitratohumulene. Absorption of the X-ray beam was neglected.

TABLE 3

Fractional atomic co-ordinates for humulene nitrosite (2), with standard deviations in parentheses

	x/a	y/b	z/c
C(1)	0.775 9(9)	0.355 4(3)	0.575 9(4)
C(2)	0.670 1(7)	0.401 6(3)	0.490 2(4)
C(3)	0.748 0(7)	0.382 8(3)	0.400 2(4)
C(4)	0.595 6(8)	0.398 0(3)	0.305 3(4)
C(5)	0.432 5(8)	0.333 8(3)	0.284 9(4)
C(6)	0.527 4(9)	0.259 2(3)	0.299 0(4)
C(7)	0.481 3(9)	0.211 1(3)	0.361 8(4)
C(8)	0.669 8(12)	0.149 5(3)	0.506 0(4)
C(9)	0.767 5(10)	0.223 2(4)	0.533 7(4)
C(10)	0.682 3(10)	0.279 2(4)	0.571 4(4)
C(11)	0.594 4(11)	0.140 9(3)	0.395 2(5)
C(12)	0.446 4(14)	0.075 1(4)	0.377 4(6)
C(13)	0.786 7(14)	0.127 0(4)	0.351 0(6)
C(14)	0.482 3(10)	0.470 9(3)	0.298 5(5)
C(15)	0.481 9(15)	0.273 8(5)	0.606 8(7)
N(1)	0.726 6(17)	0.390 3(4)	0.229 5(5)
N(2)	0.952 0(8)	0.425 7(4)	0.406 3(4)
O(1)	0.947 7(8)	0.488 4(4)	0.379 9(4)
O(2)	1.108 8(7)	0.395 0(3)	0.439 3(4)
O(3)	0.669 2(15)	0.415 8(5)	0.156 7(8)

Structure Analysis.—The crystal structures were elucidated with a version of the program MULTAN, adapted for the Glasgow University ICL 2976 computer by Dr. C. J. Gilmore.

The analyses of dinitrohumulene and nitronitratohumulene were straightforward. After preliminary adjustment of the positional and anisotropic thermal parameters of the C, N, and O atoms, the hydrogen atoms were located in difference electron-density maps and were included in the full-matrix least-squares calculations with isotropic thermal parameters. These calculations converged at R 0.042, R_w 0.048 (dinitrohumulene) and R 0.052, R_w 0.047 (nitronitratohumulene) with weights given by $w = 1/\sigma^2(|F|)$.

The calculations for humulene nitrosite posed rather more problems. The C(15)–H atoms were assigned co-ordinates from a difference map and were included as variables in the least-squares calculations but in view of the limited number of $|F_o|$ values the other H atoms were kept at ideal positions; all H atoms had $U_{iso.}$ fixed at 0.10 Å^2. Refinement with anisotropic thermal parameters for the C, N, and O atoms then converged at R 0.100, R_w 0.111 with weights given by $w = 1/[\sigma^2(|F|) + 0.000\,74|F|^2]$. A difference synthesis showed several peaks in the region of the NO group but elsewhere was acceptably flat. When the four highest peaks were included as O atoms and their occupation parameters included as variables we obtained R 0.078, R_w 0.084 and the results indicated that two of these additional 'atoms' contained only 0.16 and 0.01 electrons. Accordingly, these 'atoms' were eliminated from the calculations and further least-squares refinement converged at R 0.071, R_w 0.076 with weights given by $w = 1/[\sigma^2(|F|) + 0.000\,92|F|^2]$. The two additional 'atoms' retained in these calculations contained 2.7 and 1.5 electrons. Their presence in the crystal structure can be attributed to the presence of some dinitro- and/or nitronitrato-humulene in the nitrosite crystal or to partial decomposition of the nitrosite in the X-ray beam.

TABLE 4

Fractional atomic co-ordinates for dinitrohumulene (3), with standard deviations in parentheses

	x/a	y/b	z/c
C(1)	0.773 2(4)	0.355 0(2)	0.575 3(2)
C(2)	0.667 8(3)	0.401 6(1)	0.488 9(2)
C(3)	0.755 0(3)	0.385 0(1)	0.398 7(2)
C(4)	0.599 4(3)	0.399 0(1)	0.304 4(2)
C(5)	0.440 0(4)	0.334 0(1)	0.283 8(2)
C(6)	0.537 2(4)	0.259 5(1)	0.299 0(2)
C(7)	0.488 7(4)	0.210 7(1)	0.395 8(2)
C(8)	0.670 1(5)	0.149 6(2)	0.505 6(2)
C(9)	0.767 9(4)	0.223 0(2)	0.533 7(2)
C(10)	0.677 7(4)	0.279 2(2)	0.569 7(2)
C(11)	0.600 4(4)	0.140 9(1)	0.394 9(2)
C(12)	0.451 3(6)	0.074 3(2)	0.374 1(2)
C(13)	0.793 8(5)	0.127 5(2)	0.349 1(3)
C(14)	0.479 7(4)	0.471 4(1)	0.297 3(2)
C(15)	0.467 6(5)	0.275 4(2)	0.600 7(3)
N(1)	0.725 6(4)	0.395 6(1)	0.222 2(2)
N(2)	0.954 9(3)	0.430 5(1)	0.405 6(2)
O(1)	0.945 9(3)	0.492 7(1)	0.375 2(2)
O(2)	1.119 0(3)	0.401 5(1)	0.446 7(2)
O(3)	0.899 8(3)	0.366 3(1)	0.237 3(1)
O(4)	0.643 6(3)	0.420 4(1)	0.145 2(1)

Fourier and least-squares calculations were performed with the programs SHELX (nitronitratohumulene and humulene nitrosite) and XRAY (dinitrohumulene). Molecular diagrams were prepared with the program ORTEP.

Atomic co-ordinates are listed in Tables 3—5. Observed and calculated structure amplitudes, thermal parameters, hydrogen-atom positions, and full details of bond lengths

TABLE 5

Fractional atomic co-ordinates for nitronitratohumulene (4), with standard deviations in parentheses

	x/a	y/b	z/c
C(1)	0.878 3(4)	0.215 7(-)	0.382 8(2)
C(2)	0.822 6(3)	0.238 2(3)	0.302 0(2)
C(3)	0.628 7(3)	0.260 7(3)	0.295 5(1)
C(4)	0.574 7(3)	0.333 5(3)	0.228 3(1)
C(5)	0.623 3(3)	0.457 2(3)	0.243 4(1)
C(6)	0.565 6(3)	0.497 9(3)	0.318 0(1)
C(7)	0.674 7(3)	0.540 2(3)	0.367 4(1)
C(8)	0.766 6(4)	0.487 0(3)	0.492 3(1)
C(9)	0.776 3(3)	0.368 3(3)	0.464 0(1)
C(10)	0.901 2(3)	0.325 8(3)	0.421 8(1)
C(11)	0.639 9(3)	0.562 2(3)	0.447 9(1)
C(12)	0.677 9(5)	0.685 4(3)	0.467 0(2)
C(13)	0.452 1(4)	0.535 3(4)	0.469 5(2)
C(14)	0.643 2(4)	0.290 3(4)	0.155 3(1)
C(15)	1.068 5(4)	0.385 5(4)	0.404 2(3)
N(1)	0.273 8(3)	0.369 2(3)	0.180 9(1)
N(2)	0.532 4(3)	0.150 1(3)	0.294 5(1)
O(1)	0.566 7(4)	0.081 3(3)	0.247 9(1)
O(2)	0.422 7(4)	0.134 6(3)	0.342 2(2)
O(3)	0.122 9(3)	0.341 1(3)	0.189 2(2)
O(4)	0.332 4(3)	0.429 8(3)	0.135 2(1)
O(5)	0.381 3(2)	0.318 6(3)	0.233 5(1)

and angles are listed in Supplementary Publication No. SUP 23276 (39 pp.).*

* For details, see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 1*, 1981, Index Issue.

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