

port (Le 288/14). We thank the College of Arts and Sciences of the University of Toledo for generous financial support of the X-ray diffraction facility.

Lists of structure factors, anisotropic thermal parameters, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71365 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1067]

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1-S19.
- Armet, O., Veciana, J., Roveria, C., Riera, J., Castaner, J., Molina, E., Rius, J., Miravittles, C., Olivella, S. & Brichfeus, J. (1987). *J. Phys. Chem.* **91**, 5608-5616.
- Ballester, M. (1989). *Adv. Phys. Org. Chem.* **25**, 267.
- Ballester, M. & Rosa, J. (1960). *Tetrahedron*, **9**, 156-162.
- Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488-492.
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 154-157.
- Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902-3909.
- Enraf-Nonius (1977). *CAD-4 Operations Manual*. Enraf-Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Gali, S., Solans, X., Miravittles, C., Font-Altaba, M. & Armet, O. (1978). *Acta Cryst.* **B34**, 1011-1014.
- Gano, J. E., Lenoir, D., Park, B.-S. & Roesner, R. A. (1987). *J. Org. Chem.* **52**, 5636-5638.
- Gano, J. E., Park, B.-S., Pinkerton, A. A. & Lenoir, D. (1990). *J. Org. Chem.* **55**, 2688-2693.
- Gano, J. E., Park, B. S., Pinkerton, A. A. & Lenoir, D. (1991). *Acta Cryst.* **C47**, 162-164.
- Gano, J. E., Park, B.-S., Subramaniam, G., Lenoir, D. & Gleiter, R. (1991). *J. Org. Chem.* **56**, 4806-4808.
- Gano, J. E., Subramaniam, G. & Birnbaum, R. (1990). *J. Org. Chem.* **55**, 4760-4763.
- Gilbert, K. & Gyjewski, J. (1992). *PCModel for the Macintosh*. Version 4.0. Serena Software, Bloomington, Indiana, USA.
- Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781-782.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kaluski, Z. & Skrzypczak-Jankun, E. (1978). *Proceedings of the Pre-Congress Symposium on Organic Crystal Chemistry*, pp. 273-293. Poznań: Dymaczewo.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Miravittles, C., Molins, E., Solans, X., Germain, G. & Declercq, J.-P. (1985). *J. Incl. Phenom. Mol. Recognit. Chem.* **3**, 27-34.
- Molinet, C. (1955). MS thesis, Univ. of Madrid, Spain.
- Pedersen, B. F. (1975). *Acta Cryst.* **B31**, 2931-2933.
- Stewart, J. J. (1989a). *J. Comput. Chem.* **10**, 209-220, 221-264.
- Veciana, J., Carilla, J., Miravittles, C. & Molina, E. (1987). *J. Chem. Soc. Chem. Commun.* pp. 812-814.
- Wang, T.-L., Chen, J.-B., Xu, W.-H., Zhang, S.-W., Pan, Z.-H. & Tang, Y.-Q. (1987). *Acta Chim. Sin.* **45**, 636-644.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139-1144.

Acta Cryst. (1993). **C49**, 1988-1990

1,2,4-Trifluoro-6,8-dimethyl-3-trifluoromethylphenazine, C₁₅H₈F₆N₂, Produced via Thermolysis of Perfluoro-4-azidotoluene in the Presence of 2,4,6-Trimethylaniline

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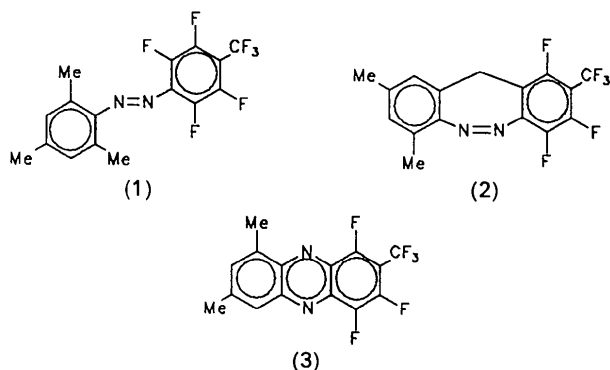
(Received 13 April 1993; accepted 8 June 1993)

Abstract

Despite extensive substitution, the dimensions of the planar phenazine rings remain very close to those of the unsubstituted molecule [Woźniak, Kariuki & Jones (1991). *Acta Cryst.* **C47**, 1113-1114]. Typically, the molecules form stacks in which fluorinated rings overlap methylated rings of adjacent molecules.

Comment

The structure determination was undertaken to establish beyond doubt the identity of unexpected products encountered during an extension (Banks & Madany, 1993) of studies on the trapping of thermally generated perfluoroaryl nitrenes with 1,3,5-trimethylbenzene (Banks & Madany, 1985) and aniline (Banks & Prakash, 1974). Formation of the azo compound (1) can be ascribed to trapping of the incipient singlet nitrene 4-CF₃C₆F₄N by the electron-rich 2,4,6-trimethylaniline (Banks & Prakash, 1974). The dibenzo[1,2]diazepine (2) is known to be produced via the thermal intramolecular dehydrofluorination of (1) (Alty, Banks, Fishwick, Pritchard & Thompson, 1984). However, just how the phenazine (3) arises is not



clear. Thermal oxidative cyclization of non-fluorinated azobenzenes to phenazines in the presence of ferrous oxalate has been reported (Abramovitch & Davis, 1968), but

the mechanism proposed is not helpful to the understanding of how the fluorinated phenazine (3) arises. Further work will be needed to resolve this matter.

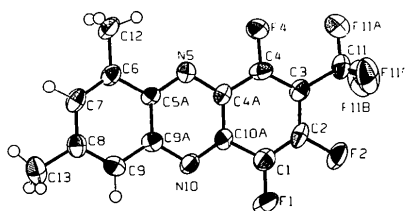


Fig. 1. The title molecule, including atomic numbering scheme, drawn using ORTEPII (Johnson, 1976).

Experimental

Crystal data

$C_{15}H_8F_6N_2$

$M_r = 330.23$

Monoclinic

$C2/c$

$a = 26.705 (4) \text{ \AA}$

$b = 7.271 (1) \text{ \AA}$

$c = 15.403 (4) \text{ \AA}$

$\beta = 118.19 (2)^\circ$

$V = 2636 (1) \text{ \AA}^3$

$Z = 8$

$D_x = 1.664 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 8.67\text{--}12.92^\circ$

$\mu = 0.1522 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate

$0.40 \times 0.20 \times 0.05 \text{ mm}$

Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction: not applied

2570 measured reflections

2524 independent reflections

838 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.059$

$\theta_{\text{max}} = 25.0^\circ$

$h = 0 \rightarrow 31$

$k = 0 \rightarrow 8$

$l = -16 \rightarrow 16$

3 standard reflections

monitored every 150

reflections

intensity variation: none

Refinement

Refinement on F

Final $R = 0.067$

$wR = 0.061$

$S = 2.483$

838 reflections

208 parameters

H-atom parameters not refined

Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\text{max}} = 0.0034$

$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

Extinction correction: not applied

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN, MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*

LS. Molecular graphics: *TEXSAN, ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} |
|------|------------|-------------|------------|-----------------|
| C1 | 0.6485 (4) | 0.594 (1) | 0.7178 (7) | 0.0464 |
| C2 | 0.6927 (4) | 0.562 (1) | 0.7013 (7) | 0.0457 |
| C3 | 0.6902 (4) | 0.576 (1) | 0.6082 (7) | 0.0390 |
| C4 | 0.6391 (4) | 0.621 (1) | 0.5320 (7) | 0.0419 |
| C4a | 0.5906 (4) | 0.661 (1) | 0.5436 (7) | 0.0381 |
| N5 | 0.5420 (3) | 0.7108 (9) | 0.4635 (5) | 0.0363 |
| C5a | 0.4978 (4) | 0.750 (1) | 0.4791 (6) | 0.0308 |
| C6 | 0.4453 (4) | 0.808 (1) | 0.3984 (6) | 0.0395 |
| C7 | 0.4018 (4) | 0.852 (1) | 0.4174 (7) | 0.0422 |
| C8 | 0.4056 (4) | 0.840 (1) | 0.5129 (7) | 0.0428 |
| C9 | 0.4552 (4) | 0.781 (1) | 0.5901 (7) | 0.0446 |
| C9a | 0.5024 (4) | 0.736 (1) | 0.5757 (7) | 0.0387 |
| N10 | 0.5518 (3) | 0.685 (1) | 0.6557 (5) | 0.0409 |
| C10a | 0.5948 (4) | 0.650 (1) | 0.6376 (6) | 0.0360 |
| C11 | 0.7422 (4) | 0.537 (2) | 0.5989 (8) | 0.0555 |
| C12 | 0.4400 (3) | 0.816 (1) | 0.2978 (6) | 0.0507 |
| C13 | 0.3554 (4) | 0.893 (1) | 0.5261 (7) | 0.0583 |
| F1 | 0.6528 (2) | 0.5813 (8) | 0.8075 (3) | 0.0628 |
| F2 | 0.7428 (2) | 0.5167 (8) | 0.7792 (4) | 0.0635 |
| F4 | 0.6324 (2) | 0.6344 (8) | 0.4403 (4) | 0.0578 |
| F11A | 0.7351 (2) | 0.5416 (10) | 0.5095 (4) | 0.0928 |
| F11B | 0.7643 (3) | 0.375 (1) | 0.6354 (5) | 0.0999 |
| F11C | 0.7832 (2) | 0.6596 (9) | 0.6508 (5) | 0.0918 |

Table 2. Geometric parameters (\AA , $^\circ$)

| | | | |
|------------|-----------|--------------|-----------|
| C1—C2 | 1.34 (1) | C5a—C6 | 1.43 (1) |
| C1—C10a | 1.44 (1) | C5a—C9a | 1.44 (1) |
| C2—C3 | 1.41 (1) | C6—C7 | 1.36 (1) |
| C3—C4 | 1.35 (1) | C7—C8 | 1.43 (1) |
| C4—C4a | 1.42 (1) | C8—C9 | 1.36 (1) |
| C4a—N5 | 1.35 (1) | C9—C9a | 1.42 (1) |
| C4a—C10a | 1.40 (1) | C9a—N10 | 1.36 (1) |
| N5—C5a | 1.341 (9) | N10—C10a | 1.328 (9) |
| C2—C1—C10a | 119.8 (9) | C5a—C6—C7 | 117.9 (8) |
| C1—C2—C3 | 124 (1) | C6—C7—C8 | 123.6 (8) |
| C2—C3—C4 | 116 (1) | C7—C8—C9 | 119.0 (9) |
| C3—C4—C4a | 123.1 (9) | C8—C9—C9a | 120.3 (9) |
| C4a—N5—C5a | 116.1 (8) | C9a—N10—C10a | 115.3 (8) |

Perfluoro-4-azidotoluene (Banks & Prakash, 1974) (2.0 g, 7.7 mmol) was heated with an excess of 2,4,6-trimethylaniline (9.5 g, 70 mmol) at 453 K under dry nitrogen for 11 h. The dark-coloured product was diluted with diethyl ether (30 cm³) and the mixture washed with 2M hydrochloric acid (2 × 150 cm³). The organic layer was dried (MgSO₄), the ether removed (rotary evaporator) and the solid residue subjected to dry-column flash chromatography (silica eluted with 60/80 petroleum ether and petroleum ether-dichloromethane mixtures). This provided the known products heptafluoro-4-(2,4,6-trimethylphenylazo)toluene (1) (Alty, Banks, Thompson, Vellis & Fishwick, 1988) and 1,3,4-trifluoro-7,9-dimethyl-2-trifluoromethyl-11H-dibenzo[*c,f*][1,2]diazepine (2) (Alty, Banks, Fishwick, Pritchard & Thompson, 1984), plus greenish yellow (mustard) needles (after recrystallization from aqueous ethanol) of the new compound 1,2,4-trifluoro-6,8-dimethyl-3-trifluoromethylphenazine (3) (0.8 g, 2.4 mmol, 31% yield); m.p. 419–421 K, m/z 330 (M^+ , 100%).

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71383 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1060]

References

- Abramovitch, R. A. & Davis, B. A. (1968). *J. Heterocycl. Chem.* **5**, 793–798.
- Alty, A. C., Banks, R. E., Fishwick, B. R., Pritchard, R. G. & Thompson, A. R. (1984). *J. Chem. Soc. Chem. Commun.* pp. 832–833.
- Alty, A. C., Banks, R. E., Thompson, A. R., Vellis, H. S. & Fishwick, B. R. (1988). *J. Fluorine Chem.* **40**, 147–169.
- Banks, R. E. & Madany, I. M. (1985). *J. Fluorine Chem.* **30**, 211–226.
- Banks, R. E. & Madany, I. M. (1993). In preparation.
- Banks, R. E. & Prakash, A. (1974). *J. Chem. Soc. Perkin Trans. 1*, pp. 1365–1371.
- Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Wozniak, K., Kariuki, B. & Jones, W. (1991). *Acta Cryst.* **C47**, 1113–1114.

Acta Cryst. (1993). **C49**, 1990–1992

Ceratiolin from *Ceratiola ericoides*

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(Received 23 December 1992; accepted 20 April 1993)

Abstract

The title compound, 3-phenyl-1-(2,4,5-trihydroxy-3,5-dimethyl-6-oxo-1,5-cyclohexadienyl)-1-propanone, was confirmed to be a dihydrochalcone containing a fully substituted cyclohexadienone ring. This ring has a flattened half-chair conformation, with the dione C atom 0.203 (1) Å out of the diene plane and the tetrahedral C atom 0.184 (1) Å to the opposite side of the plane. The hydroxy substituent on the tetrahedral C atom forms an intramolecular hydrogen bond to the carbonyl O atom of the cyclohexadienone, having an O...O distance of 2.658 (1) Å and an angle at H of 116 (2)°. One of the other hydroxy substituents forms an intramolecular hydrogen bond

with the carbonyl O atom of the β -phenylpropionyl group, having an O...O distance of 2.414 (2) Å and an angle at H of 160 (2)°.

Comment

The title compound is an external leaf constituent of false rosemary (*Ceratiola ericoides*, Empetraceae), which is endemic to the Florida scrub. There exists strong evidence that the ecological role of the non-active ceratiolin lies in its photochemical decomposition into β -phenylpropionic acid, which is a potent selective allelopathic agent for native Florida grasses (Fischer, Tanrisever & Williamson, 1988). The structure of ceratiolin was initially inferred from NMR, mass spectral and chemical data (Tanrisever, Fronczek, Fischer & Williamson, 1987). Although its structure was later verified by total synthesis (Obara, Onodera, Yusa, Tsuchiya & Matsuba, 1989), the initial structure elucidation was based partially on biogenetic considerations, which left some structural uncertainties. This fact, together with the presence of the unusual cyclohexadienone moiety in ceratiolin, led us to determine its crystal structure.

The conformation of the β -phenylpropionyl substituent is described by three torsion angles. That about the central C8—C9 bond is *anti*, while the C9—C8—C7—O5 torsion angle is more nearly orthogonal [102.4 (2)°], as is that defining the conformation of the phenyl group relative to the propionyl group, C8—C9—C10—C11 [69.8 (2)°]. The first intramolecular hydrogen bond described in the *Abstract*, O2—H...O1, is actually bifurcated, the second component being intermolecular, and also with carbonyl O1 (at $-x, 1-y, 1-z$) as acceptor. The O...O distance in this contact is 2.875 (1) Å, and the angle about H is 147 (2)°. Another intermolecular O—H...O hydrogen bond exists, with O3 as donor and hydroxy O2 (at $1-x, 1-y, 1-z$) as acceptor. This contact has an O...O distance of 2.677 (1) Å and an angle at H of 151 (2)°. This hydrogen bond may also be considered to be bifurcated, with an intramolecular component, O3...O2 2.719 (1) Å, O—H...O 107 (2)°.

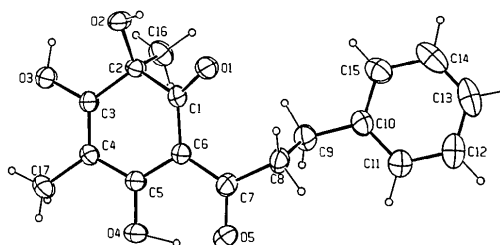


Fig. 1. ORTEP (Johnson, 1965) drawing of the title compound, with thermal ellipsoids drawn at the 40% probability level.