Refinement

Refinement on F^2
$R(F) = 0.0419$
$wR(F^2) = 0.1181$
$S = 1.029$
3103 reflections
218 parameters
H atoms freely refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.2214P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.149$ e Å^{-3}
$\Delta\rho_{min} = -0.165$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	U_{eq}
O1	0.5489 (3)	0.6584 (2)	0.40420 (11)	0.0626 (5)
O2	0.1972 (3)	0.6311 (2)	0.48825 (12)	0.0687 (5)
C1	0.3640 (3)	0.9838 (2)	0.27865 (13)	0.0404 (5)
C2	0.5198 (4)	1.0752 (3)	0.3318 (2)	0.0545 (6)
C3	0.3332 (5)	1.2246 (3)	0.3615 (2)	0.0614 (6)
C4	0.1182 (4)	1.2628 (2)	0.2886 (2)	0.0515 (5)
C5	0.0933 (6)	1.4462 (3)	0.2231 (2)	0.0729 (8)
C6	0.3092 (6)	1.4409 (3)	0.1478 (2)	0.0755 (8)
C7	0.3375 (5)	1.2613 (3)	0.1242 (2)	0.0577 (6)
C8	0.1534 (5)	1.2307 (3)	0.0518 (2)	0.0685 (7)
C9	0.0960 (4)	1.0732 (3)	0.13260 (15)	0.0532 (6)
C10	0.2846 (5)	0.9173 (3)	0.1249 (2)	0.0607 (6)
C11	0.4427 (4)	0.8777 (3)	0.1976 (2)	0.0535 (6)
C12	0.2110 (3)	1.1405 (2)	0.21572 (13)	0.0415 (5)
C13	0.2047 (4)	0.8798 (3)	0.3597 (2)	0.0478 (5)
C14	0.3374 (4)	0.7121 (3)	0.41852 (14)	0.0454 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C14	1.209 (2)	C5—C6	1.519 (4)
O2—C14	1.310 (2)	C6—C7	1.516 (3)
C1—C11	1.513 (3)	C7—C8	1.554 (3)
C1—C12	1.527 (3)	C7—C12	1.594 (3)
C1—C2	1.529 (3)	C8—C9	1.540 (3)
C1—C13	1.546 (3)	C9—C10	1.512 (3)
C2—C3	1.550 (3)	C9—C12	1.560 (3)
C3—C4	1.564 (3)	C10—C11	1.323 (3)
C4—C12	1.529 (3)	C13—C14	1.514 (3)
C4—C5	1.533 (3)		
C11—C1—C12	100.02 (15)	C1—C12—C4	106.21 (15)
C11—C1—C2	128.0 (2)	C1—C12—C9	106.72 (15)
C12—C1—C2	100.1 (2)	C4—C12—C9	134.9 (2)
C11—C1—C13	107.4 (2)	C1—C12—C7	119.2 (2)
C12—C1—C13	110.8 (2)	C4—C12—C7	103.0 (2)
C2—C1—C13	109.2 (2)	C9—C12—C7	86.78 (15)

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PEANUT* (Hummel, Hauser & Bürgi, 1990). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Grieco, P. A., Brandes, E. B., McCann, S. & Clark, J. D. (1989). *J. Org. Chem.* **54**, 5849–5851.

Guidetti-Grept, R. (1994). PhD thesis, University of Bern, Switzerland.

Hirschi, D., Luef, W., Gerber, P. & Keese, R. (1992). *Helv. Chim. Acta*, **75**, 1897–1908.

Hummel, W., Hauser, J. & Bürgi, H.-B. (1990). *J. Mol. Graph.* **8**, 214–220.

Luef, W. & Keese, R. (1992). *J. Mol. Struct. (Theochem.)*, **257**, 353–368.

Luef, W. & Keese, R. (1993). *Advances in Strain in Organic Chemistry*, Vol. 3, edited by B. Halton, pp. 229–267. Greenwich, Ct: JAI Press Ltd.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *XSCANS Users Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

3a,7a-Dibromo-2-butyl-4,7-methano-1,3,3a,4,7,7a-hexahydro-2H-isoindole-1,3-dione from the Reaction of 3,4-Dibromo-1-butylmaleimide with Cyclopentadiene

Roy L. Beddoes, Yuekun Zhao and John A. Joule*

Chemistry Department, The University of Manchester, Manchester M13 9PL, UK. E-mail: j.a.joule@man.ac.uk
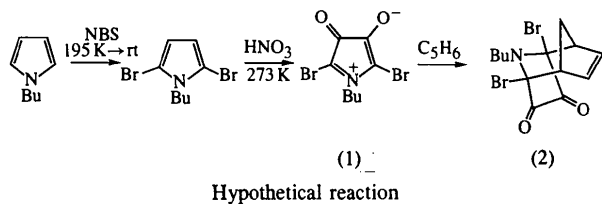
Abstract

It is shown that reaction of 1-butylpyrrole successively with *N*-bromosuccinimide then nitric acid gives 3,4-dibromo-1-butylmaleimide since the latter then undergoes Diels–Alder cycloaddition with cyclopentadiene to give the title compound, $C_{13}H_{15}Br_2NO_2$.

Comment

Interest in the cycloaddition reactions of oxidopyraziniums (Yates, Peters, Beddoes, Scopes, & Joule, 1995) drew our attention to the recent report (Brockmann

& Tour, 1995) of the apparently similar reactivity of the compound $C_8H_9Br_2NO_2$, assigned the zwitterionic structure (1), and prepared from 1-butylpyrrole by dibromination then oxidation (see scheme below). It seemed surprising the substance was recrystallized from ethanol without suffering displacement of bromine(s) by the nucleophilic solvent.
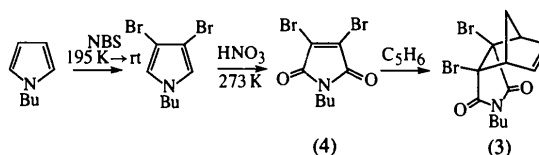

(1) (2)

Hypothetical reaction

$C_8H_9Br_2NO_2$ reacted with cyclopentadiene giving a 1:1 adduct assigned structure (2) (or its *exo* isomer). On the face of it, this thermal cycloaddition seemed to involve the symmetry-forbidden reaction of two 4π components. It seemed that the structure and relative stereochemistry of the cyclopentadiene adduct, and by implication of $C_8H_9Br_2NO_2$, could be verified by X-ray crystallographic study.

We repeated the preparation of $C_8H_9Br_2NO_2$ and the cyclopentadiene adduct derived from it, in each case obtaining materials with the same m.p. and spectroscopic properties as those reported. We have also obtained crystallographically suitable crystals of the cycloadduct by recrystallization from CH_2Cl_2/C_6H_{14}, m.p. 394–395 K.

The structure elucidation described below shows the adduct to have structure (3). This result implies that the bromination/oxidation product from 1-butylpyrrole actually has structure (4) and that the reaction with cyclopentadiene is a straightforward Diels–Alder reaction, showing normal *endo* selectivity, between the diene and the 3,4-dibromomaleimide (4) as a dienophile.

This result also implies, unless one supposes that rearrangements of both 2- and 5-bromine substituents occur during oxidation, that the bromination product is actually 3,4-dibromo-1-butylpyrrole and not its 2,5-dibromo isomer, and that the sequence is correctly represented by the scheme below. There is a precedent (Bray, Mathies, Naef, Solas, Tidwell, Artis & Muchowski, 1990) for the alteration of the normal tendency for α-electrophilic substitution in pyrroles to β-selectivity when a nitrogen substituent of substantial size is present.

(4) (3)

Experimental

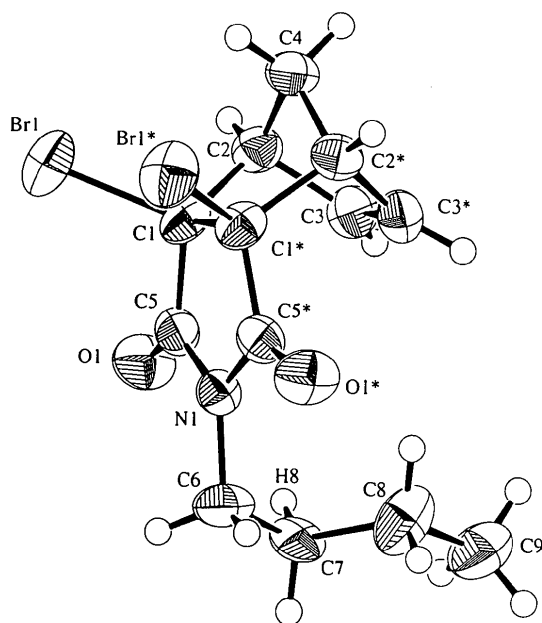Chemical synthesis and crystallization were from a mixture of dichloromethane and hexane.

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule with ellipsoids at the 50% probability level. The molecule lies on a crystallographic mirror plane, through N1, C6 and C9; the alternative positions for the disordered atoms C7 and C8, on opposite sides of this mirror plane, are not shown.

Crystal data

$C_{13}H_{15}Br_2NO_2$	Mo $K\alpha$ radiation
$M_r = 377.08$	$\lambda = 0.7107$ Å
Orthorhombic	Cell parameters from 25
$Pnma$	reflections
$a = 20.345\,(3)$ Å	$\theta = 7.7–12.1°$
$b = 10.316\,(2)$ Å	$\mu = 5.969$ mm^{-1}
$c = 6.482\,(1)$ Å	$T = 295.2$ K
$V = 1360.5\,(7)$ Å^3	Prismatic
$Z = 4$	$0.13 \times 0.12 \times 0.05$ mm
$D_x = 1.841$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Rigaku AFC-5R diffractometer	637 observed reflections $[I > 3\sigma(I)]$
ω scans	$\theta_{max} = 25.03°$
Absorption correction:	$h = 0 \rightarrow 24$
ψ scans (North, Phillips & Mathews, 1968)	$k = 0 \rightarrow 12$
$T_{min} = 0.639$, $T_{max} = 1.000$	$l = -7 \rightarrow 0$
1449 measured reflections	3 standard reflections monitored every 150 reflections
1449 independent reflections	intensity decay: -0.59%

Refinement

Refinement on F	$\Delta\rho_{max} = 0.34$ e Å^{-3}
$R = 0.0371$	$\Delta\rho_{min} = -0.36$ e Å^{-3}
$wR = 0.0245$	Extinction correction: none

$S = 1.477$
637 reflections
97 parameters
H-atom parameters not
refined
$w = 1/[\sigma^2(F_o)]$
$(\Delta/\sigma)_{max} = 0.009$

Atomic scattering factors
from *International Tables
for Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.1 for C, Br, N and O
atoms, and Table 6.1.1.2
for H atoms)

Table 1. *Fractional atomic coordinates and equivalent
isotropic displacement parameters ($\mathring{A}^2$)*

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

	x	y	z	U_{eq}
Br1	0.19925 (4)	0.08695 (7)	0.1245 (1)	0.0637 (3)
O1	0.0467 (2)	0.0301 (4)	0.2114 (8)	0.059 (2)
N1	0.0351 (4)	1/4	0.179 (1)	0.038 (3)
C1	0.1359 (3)	0.1747 (6)	0.300 (1)	0.042 (2)
C2	0.1510 (3)	0.1425 (7)	0.531 (1)	0.044 (2)
C3	0.0912 (3)	0.1859 (6)	0.650 (1)	0.048 (2)
C4	0.1989 (5)	1/4	0.583 (1)	0.051 (4)
C5	0.0686 (3)	0.1367 (7)	0.225 (1)	0.040 (2)
C6	−0.0326 (5)	1/4	0.100 (2)	0.057 (4)
C7*	−0.0818 (8)	0.199 (2)	0.266 (3)	0.056 (6)
C8*	−0.0896 (9)	0.299 (2)	0.429 (3)	0.066 (7)
C9	−0.1368 (5)	1/4	0.600 (2)	0.071 (5)

* Site occupancy 0.5.

Table 2. *Selected geometric parameters ($\mathring{A}$, °)*

Br1—C1	1.942 (6)	C2—C3	1.508 (9)
O1—C5	1.190 (7)	C2—C4	1.513 (9)
N1—C5	1.384 (7)	C3—C3^i	1.32 (1)
N1—C6	1.47 (1)	C6—C7	1.56 (2)
C1—C1^i	1.55 (1)	C7—C8	1.49 (2)
C1—C2	1.566 (9)	C8—C9	1.55 (2)
C1—C5	1.506 (9)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

The molecule has been treated as lying on a crystallographic mirror plane, with a disordered *n*-butyl substituent, in preference to the corresponding ordered space group, $Pn2_1a$, in which refinement became ill-conditioned.

Data collection: *MSC/AFC* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1163). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343.
Bray, B. L., Mathies, P. H., Naef, R., Solas, D. R., Tidwell, T. T., Artis, D. R. & Muchowski, J. M. (1990). *J. Org. Chem.* **55**, 6317–6328.
Brockmann, T. W. & Tour, J. M. (1995). *J. Am. Chem. Soc.* **117**, 4437–4447.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation. (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Yates, N. D., Peters, D. A., Beddoes, R. L., Scopes, D. I. C. & Joule, J. A. (1995). *Heterocycles*, **40**, 331–347.

5,15-Diaza-6,16-dihydroxytetrabenzo-[b,e,k,n]perylene

JIN MIZUGUCHI

Department of Chemistry, School of Education, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, 240 Yokohama, Japan. E-mail: mizuj@ed.ynu.ac.jp

Abstract

The molecule of the title compound, $C_{34}H_{18}N_2O_2$, belongs to point group C_i. The area between the two opposing phenyl rings is overcrowded so that each phenyl ring is bent out of the diazaperylene skeleton in such a way that one ring is above and the other is below the molecular plane. Due to the ring strain thus induced, the C—C bonds in the bent phenyl rings are no longer equal. There are intramolecular hydrogen bonds between the OH groups and N atoms, which stabilize the molecule. The molecules are stacked in a herringbone fashion, with an interplanar distance of 3.43 (1) $\mathring{A}$ along the *b* axis where there are close interatomic contacts.

Comment

5,15-Diaza-6,16-dihydroxytetrabenzo[*b,e,k,n*]perylene (DDTP), (I), is a new purple–violet light-stable insoluble pigment based on the diazaperylene skeleton. Kitahara, Nishi, Hasegawa & Maeda (1988) prepared it from diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate and 2-aminobenzophenone and claimed a patent with a keto structure. The colour of the pigment was reddish purple. Kitahara & Nishi (1988) later reported the synthesis and properties of diazaperylene derivatives. They proposed three possible structures, namely, an enol structure, (I), a keto structure and 5,15-diaza-5b,15b-dihydro-tetrabenzo[*b,e,k,n*]perylene-6,16-dione. From these they selected the last structure, since they could not observe the NH and OH stretching bands in the IR spectra. Jaffe (1991) independently prepared the same substance