seen in a dibromoboryl–phenanthroline compound (Klebe & Tranqui, 1984). This lengthening may help to explain the thermal instability of 4-bromopyrazabole relative to the two symmetrical compounds pyrazabole and 4,8-dibromopyrazabole (Hanecker, Hodgkins, Niedenzu & Nöth, 1985). Also, the two kinds of B—N bonds in 4-bromopyrazabole are of distinctly different lengths: N_2BHBr 1.530 (6) Å average; N_2BH_2 1.562 (7) Å average. The latter B—N bonds are similar to those observed in pyrazabole, 1.553 (3) Å. The B—N bonds in the tetrabromo compound are 1.521 (12) Å. Thus the B atoms in these three compounds should be ranked in order of increasing Lewis acidity as: N_2BH_2, N_2BHBr, N_2BBr_2. Similar reasoning has been invoked to explain trends in B—N bond lengths in other B-halopyrazaboles (Clarke, Das, Hanecker, Mariategui, Niedenzu, Niedenzu, Nöth & Warner, 1987; Hanecker, Hodgkins, Niedenzu & Nöth, 1985).

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Structure of 1-Morpholinoanthraquinone at 110 K*

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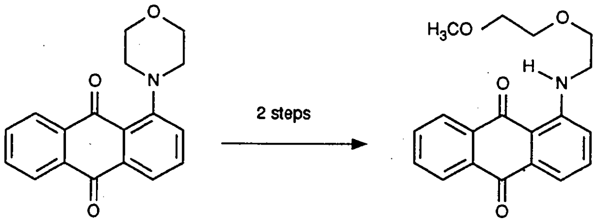
Abstract. $C_{18}H_{15}NO_3$, $M_r = 293.3$, monoclinic, $P2_1/a$, $a = 12.456$ (2), $b = 6.735$ (4), $c = 16.135$ (3) Å, $\beta = 92.17$ (1)°, $V = 1353$ Å^3, $Z = 4$, $D_x(110\ \mathrm{K}) = 1.440$, $D_x(295\ \mathrm{K}) = 1.387$, $D_m(295\ \mathrm{K}) = 1.380$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.90$ cm^{-1}, $T = 110$ K, $F(000) = 616$, final $R = 0.034$, 1889 unique reflections. A repulsive interaction between the morpholine moiety and the carbonyl oxygen (O9) is observed, which distorts the angles O9—C9—C9a [123.3 (1)°] and N1—C1—C9a [122.0 (1)°]. Both O9 and to a lesser extent O10 are bent out of the anthraquinone plane, but in opposite directions.

Introduction. The title compound 1-morpholinoanthraquinone (I) was synthesized as a precursor to the anthraquinone-based podand (II) which is related to previously synthesized anthraquinone-based lariat ethers (Gustowski, Delgado, Gatto, Echegoyen & Gokel, 1986*a*,*b*; Echegoyen, Yoo, Gatto, Gokel & Echegoyen, 1989). In the course of those investigations we found that (I) is about four orders of magnitude more basic than (II) (Kaufmann, 1991).



(I) (II)

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* This structure was solved in an introductory class to X-ray crystallography.

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It is known that anthraquinones with an NH*R* group in position 1 (Fig. 1) form an intramolecular hydrogen bond to the neighbouring carbonyl oxygen. The structure analyses of 1-[2-(diethylamino)ethylamino]anthraquinone (III) (Almond, Cutbush, Islam, Kuroda & Neidle, 1983) and 1-[(4-dimethylaminophenyl)amino]anthraquinone (IV) (Foitzik & Paulus, 1986), the only monosubstituted anthraquinones having an amino group in position 1, have shown that the N, the amino H and the first C of the alkyl residue are almost coplanar with the anthraquinone unit. This geometry allows maximum overlap of the N lone pair with the electron-deficient aromatic nucleus and thus a low basicity is expected. The goal of the present work was to obtain information about the molecular structure of (I) in order to explain its increased basicity. No structure of a doubly N-substituted 1-aminoanthraquinone has been determined so far.

Experimental. The material was dissolved in boiling toluene and the hot solution filtered. On cooling, dark red crystals separated. Their identity was confirmed by nuclear magnetic resonance spectroscopy and elemental analysis. The fragment to be measured (approx. 0.4 × 0.35 × 0.3 mm) was cut from a platelet that was smaller and more regular than the large specimens of which the batch was mainly composed. D_m was measured by flotation in a mixture of saturated aqueous NaBr and KBr solutions. 3083 diffraction intensities ($-16 \le h \le 16$, $0 \le k \le 8$, $0 \le l \le 20$, ω-scan mode) were recorded on an Enraf–Nonius CAD-4 diffractometer with low-temperature attachment using graphite-monochromated Mo $K\alpha$ radiation to $[(\sin\theta)/\lambda]_{\max} = 0.64$ Å^{-1} ($\theta_{\max} = 27°$). Cell parameters were refined from 19 reflections within the range $8.2 \le \theta \le 24.9°$. The intensities of three standard reflections ($5\bar{2}\bar{2}$, $\bar{5}22$, $\bar{1}000$, measured every 77 reflections), showed a decrease of 3.4% during the experiment (exposure time 92 h). Data reduction was carried out with the *SDP* program (B. A. Frenz & Associates, Inc., 1983). Data were corrected for decay, Lorentz and polarization effects, no absorption correction was applied. Equivalent reflections were merged ($R_{\rm int} = 0.0413$), and reflections inconsistent with reflection conditions rejected. Of the remaining 2676 unique reflections, 1889 with $F > 6\sigma(F)$ were considered observed. The structure was solved using the direct-methods package *SHELXS*86 (Sheldrick, 1985). 201 parameters were refined by full-matrix least squares on *F* with *SHELX*76 (Sheldrick, 1976). Non-H atoms were refined anisotropically, H atoms isotropically using a riding model with C—H = 0.98 Å. The final weighting scheme was $w = 1.1090[\sigma^2(F) + 0.0004(F^2)]^{-1}$. $R = 0.034$, $wR = 0.044$, GOF = 1.608, max. shift/e.s.d. = 0.031, max. peak and min. trough in final ΔF synthesis were 0.22 (C8a—C10a bond) and -0.22 e Å^{-3} (centre of benzene ring C5—C8, C8a, C10a). Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates and equivalent isotropic displacement parameters are given in Table 1.*

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* $B_{\rm eq}$ (Å$^2 \times 10^2$)

$$B_{\rm eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O9	9798 (1)	816 (2)	3244 (1)	180 (2)
O10	11221 (1)	−628 (2)	210 (1)	177 (2)
O13	8547 (1)	−3544 (2)	5025 (1)	188 (2)
N1	8971 (1)	−3038 (2)	3322 (1)	124 (2)
C1	9244 (1)	−3058 (2)	2492 (1)	120 (3)
C2	8849 (1)	−4575 (3)	1971 (1)	147 (3)
C3	9095 (1)	−4664 (3)	1143 (1)	164 (3)
C4	9771 (1)	−3267 (3)	816 (1)	149 (3)
C4a	10175 (1)	−1733 (2)	1308 (1)	121 (2)
C5	11932 (1)	2853 (3)	1019 (1)	135 (3)
C6	12336 (1)	4427 (3)	1485 (1)	159 (3)
C7	12074 (1)	4615 (3)	2312 (1)	176 (3)
C8	11378 (1)	3283 (3)	2663 (1)	147 (3)
C8a	10950 (1)	1708 (2)	2194 (1)	114 (2)
C9a	9893 (1)	−1546 (2)	2147 (1)	112 (2)
C9	10181 (1)	326 (2)	2588 (1)	122 (2)
C10	10901 (1)	−308 (2)	903 (1)	123 (3)
C10a	11257 (1)	1464 (2)	1377 (1)	115 (2)
C11	9837 (1)	−3034 (3)	3961 (1)	140 (3)
C12	9407 (1)	−2318 (3)	4767 (1)	160 (3)
C14	7711 (1)	−3569 (3)	4402 (1)	176 (3)
C15	8097 (1)	−4309 (3)	3580 (1)	156 (3)

Discussion. Fig. 1 shows (I) with atomic labels (IUPAC convention for anthraquinone). Both carbonyl bonds are bent out of the least-squares plane defined by the carbons C1 to C4, C4a and C9a, the vertical displacements being largest for O9 and C9, somewhat smaller for O10 and C10, and smallest for N1 (Table 2). The angles O9—C9—C9a, O9—C9—C8a [123.3 (1) *vs.* 118.5 (1)°] and N1—C1—C9, N1—C1—C2 [122.0 (1) *vs.* 119.4 (1)°] indicate that the bonds C9═O9 and C1—N1 are splayed apart, as they are in (III) and (IV). H112 approaches O1 to about 2.3 Å, which is 0.3 Å shorter than the sum of the van der Waals radii. The opposite direction of the O9 and N1 displacements perpendicular to the anthraquinone plane and the short O9—H112 contact distance indicate steric repulsion between O9 and the morpholine. The N1—C1 bond is shorter [1.394 (2) Å] than the N1—C11 and N1—C14 bonds [both 1.458 (2) Å], the angles C11—N1—C1, C14—N1—C1 and C11—N1—C14 are 118.5 (1), 118.7 (1)

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* Lists of structure factors, H-atom coordinates and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54919 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0291]

and 109.8 (1)°, and N1 is at a distance of 0.30 Å from the C1—C11—C14 plane. These parameters indicate considerable double-bond character for N1—C1. Still, C1—N1 at 110 K is longer than the same bonds in (III) and (IV) at room temperature [(III) 1.356 (4) Å, 298 K; (IV) 1.358 Å as computed from the data of Foitzik & Paulus, 297 K]. If it is assumed that the N1 lone pair lies in the plane bisecting the angle C11—N1—C14 and that the C1 *p* orbital is perpendicular to the N1—C1—C9a plane, the lone-pair *p*-orbital torsion angle computes to approximately 21°, whereas the same angle in (II), (III) and (IV) would be close to 0°. The conformation of the morpholine subunit relative to the anthraquinone is thus a compromise between electronic and steric effects, so that the N1 lone pair points somewhat in the direction of the O9 lone pair instead of overlapping optimally with the aromatic system. This may account for the increased basicity of (I) as compared to (II). Similar phenomena have been found with 1,8-bis(dialkylamino)naphthalenes [the so-called 'proton sponges' (Alder, Bowman, Steele & Winterman, 1968; Staab & Saupe, 1988)]. Additional angles and distances are given in Table 3.

Fig. 2 shows the packing of the molecule in the unit cell. The packing consists of double layers of morpholine and anthraquinone units that alternate in the **c** direction. Nearest pairs of molecules related by symmetry centres at (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,0) point with their O10 atoms towards each other. The intermolecular distances O10—O10′ and O10—C10′ are 3.20 Å, while O10—C4′ is 3.34 Å. These distances are considered small enough to cause intermolecular crowding (Onuma & Ijiima, 1990) and therefore induce deformations of the molecules. In fact, the out-of-plane bending of O10 and C10 is such as to increase nonbonded distances.

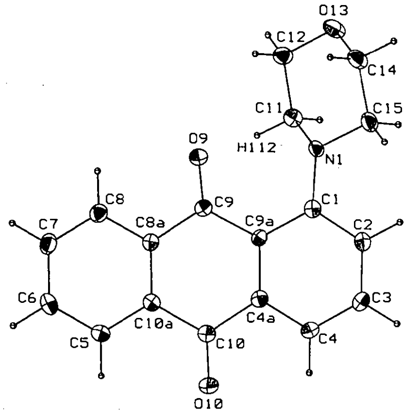

Fig. 1. View of 1-morpholinoanthraquinone (I), with thermal ellipsoids representing 50% probability density (110 K).

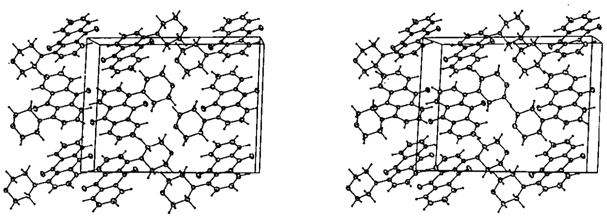

Fig. 2. Stereoscopic view of molecular packing of (I).

Table 2. *Distances* (Å) *out of the best plane defined by the atoms* C1–C4, C4a *and* C9a *of* 1-*morpholinoanthraquinone*

Equation of the plane [orthogonal coordinates (Å)]*
$-0.803X + 0.552Y - 0.226Z = -11.160$

C1	−0.020 (2)	C5	0.059 (4)
C2	−0.004 (2)	C6	0.076 (5)
C3	0.021 (2)	C7	0.104 (5)
C4	−0.008 (2)	C8	0.168 (4)
C4a	−0.016 (2)	C8a	0.176 (3)
C9a	0.027 (2)	C10a	0.079 (3)
O9	0.601 (3)	N1	−0.045 (2)
C9	0.278 (3)	C11	−1.131 (3)
O10	−0.239 (3)	C12	−0.733 (4)
C10	−0.056 (3)	C14	0.610 (4)
C15	0.252 (3)		
O13	−0.434 (4)		

* *X* parallel to *b*⊗*c*; *Y*, *Z* parallel to *b*, *c* respectively.

Table 3. *Interatomic distances* (Å) *and angles* (°) *for* 1-*morpholinoanthraquinone*

O13—C12	1.427 (2)	C4a—C10	1.487 (2)
O13—C14	1.420 (2)	C5—C6	1.383 (2)
O9—C9	1.223 (2)	C5—C10a	1.397 (2)
O10—C10	1.220 (2)	C6—C7	1.391 (2)
N1—C1	1.394 (2)	C7—C8	1.384 (2)
N1—C11	1.463 (2)	C8—C8a	1.397 (2)
N1—C15	1.458 (2)	C8a—C9	1.495 (2)
C1—C2	1.401 (2)	C8a—C10a	1.396 (2)
C1—C9a	1.426 (2)	C9—C9a	1.485 (2)
C2—C3	1.383 (2)	C10—C10a	1.477 (2)
C3—C4	1.381 (2)	C11—C12	1.504 (2)
C4—C4a	1.386 (2)	C14—C15	1.512 (2)
C4a—C9a	1.417 (2)		
C12—O13—C14	109.8 (1)	C8—C8a—C10a	119.2 (1)
C1—N1—C11	118.5 (1)	C9—C8a—C10a	122.1 (1)
C11—N1—C15	109.8 (1)	C1—C9a—C4a	118.3 (1)
C1—N1—C15	118.7 (1)	C1—C9a—C9	123.3 (1)
N1—C1—C2	119.4 (1)	C4a—C9a—C9	118.0 (1)
N1—C1—C9a	122.0 (1)	O9—C9—C8a	118.5 (1)
C2—C1—C9a	118.6 (1)	O9—C9—C9a	123.3 (1)
C1—C2—C3	121.7 (2)	C8a—C9—C9a	118.2 (1)
C2—C3—C4	120.0 (2)	O10—C10—C4a	120.9 (1)
C3—C4—C4a	120.2 (1)	O10—C10—C10a	121.0 (1)
C4—C4a—C10	116.3 (1)	C4a—C10—C10a	118.0 (1)
C4—C4a—C9a	121.1 (1)	C5—C10a—C10	120.0 (1)
C9a—C4a—C10	122.6 (1)	C8a—C10a—C10	119.8 (1)
C6—C5—C10a	120.0 (1)	C5—C10a—C8a	120.1 (1)
C5—C6—C7	119.8 (1)	N1—C11—C12	109.4 (1)
C6—C7—C8	120.5 (2)	O13—C12—C11	111.3 (1)
C7—C8—C8a	120.2 (1)	O13—C14—C15	112.1 (1)
C8—C8a—C9	118.7 (1)	N1—C15—C14	108.8 (1)

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Molecular Co-Crystals of Carboxylic Acids. 8.* Structure of the 1:1 Adduct of 3,5-Dinitrobenzoic Acid with 3-Amino-1*H*-1,2,4-triazole

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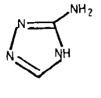
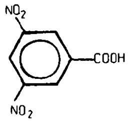
Abstract. $C_7H_3N_2O_6^-.C_2H_5N_4^+.2H_2O$, $M_r = 332.1$, triclinic, $P\bar{1}$, $a = 7.087\ (5)$, $b = 10.330\ (6)$, $c = 10.473\ (7)$ Å, $\alpha = 111.76\ (3)$, $\beta = 93.55\ (4)$, $\gamma = 95.89\ (4)°$, $V = 704.2\ (8)$ Å^3, $Z = 2$, $D_x = 1.566$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.15$ mm^{-1}, $F(000) = 344$, $T = 295$ K, $R = 0.035$ for 1656 observed reflections. The compound was prepared in toluene with crystals grown from aqueous ethanol. The two organic molecules associate to form an eight-membered hydrogen-bonded ring [NH···O, 2.88 (1) and 2.67 (1) Å], as well as being involved in a hydrogen-bonded network with two water molecules.

Introduction. 3-Amino-1,2,4-triazole, or amitrole (CA Registry No. 61-82-5) (3-AT), is a herbicide that is readily absorbed by roots and aerial plant parts, inducing chlorosis and causing eventual death of the plants. It reacts with most acids and bases to form salts, and it also reacts with ketones and aldehydes to form derivatives of possible biological activity (Spencer, 1973). 3,5-Dinitrobenzoic acid (DNBA) has been successfully adducted with various other acids and bases (Lynch, Smith, Byriel & Kennard, 1991*a*,*b*), in particular with another biologically important compound, indole-3-acetic acid. The structures of DNBA (Colapietro, Domenicano, Marciante & Portalone, 1983) and 3-AT (Starova, Frank-Kamenetskaya, Makarskii & Lopirev, 1978) are known, so comparisons of structural features with those of the co-crystal adducts can be made.



3-AT



DNBA

Experimental. The title compound was prepared by refluxing equimolar amounts of 3,5-dinitrobenzoic acid and 3-aminotriazole in toluene for 20 min at 423 K. The yellow product obtained after evaporation to dryness was recrystallized from 50% aqueous ethanol, yielding yellow prisms. A crystal with dimensions 0.23 × 0.14 × 0.40 mm was used to collect data at 295 K on an Enraf–Nonius CAD-4 four-circle diffractometer using graphite-monochromated Mo $K\alpha$ X-radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained using angle data from 25 reflections with $2\theta < 50°$. Data collection details: $2\theta/\omega$ collection mode, variable scanning rate; $2\theta_{\max}$ 50°; collection range h 0 to 8, k −12 to 12, l −12 to 12; total data 2699; 2229 unique (R_{int} 0.0123); 747 unobserved data; variation of three standards (136,

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* Part 7: Lynch, Smith, Byriel & Kennard (1992).

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