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Synthesis and X-ray structural characterization of indoaniline dye carrying a monoazacrown moiety

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Abstract

An indoaniline dye carrying a monoazacrown moiety was prepared by condensation of 10-(4′-nitrosophenyl)-1,4,7-trioxa-10-azacyclododecane with α-nahpthol. The crystal structure was determined by X-ray crystallography and the crystal was found to exist in the monoclinic space group $P2_1/c$ (No. 14). Results showed that this dye is non-planar, with a dihedral angle of 36.53° between the quinonimine and aniline moieties. In the crystal, two different streoisomers are stacked alternately.

Keywords: Keywords; Indoaniline dye; Monoazacrown; Crystal structure; Molecular orbital calculation

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1. Introduction

Indoaniline dyes are blue in colour and are typical donor–acceptor chromogens. The indoaniline dye (**1a**) can be prepared by condensing α-naphthol with *p*-nitroso-dimethylaniline, or by the oxidation (e.g. with dichromate and acetic acid) of a mixture of α-naphthol and *p*-aminodimethylaniline. The corresponding leuco compound in alkaline solution has substantivity towards cotton and so indoaniline was used at one time as a vat dye. Such indoanilines are solvent soluble dyes which are not now used for textile coloration, but enjoy usage in colour photography and also serve as intermediates for sulfur dyes.

In recent years, the synthesis of indonaphthol IR-absorbing functional dyes has been the subject of development because such dyes are of interest for use in optical information recording media. The application of the PPP MO method to the molecular design of such dyes indicates that the introduction of acceptor groups into the quinone moiety and/or of donor groups into the aniline moiety should produce a bathochromic shift of the absorption band.

4-(4′-*N,N*-Dialkylamino)phenylimino-2,3-dicyano-1,4-naphthoquinone (**1b**) and its structural analogues have been synthesized by Kim et al. [1]; dye **1b** absorbs at 795 nm in trichloromethane. Replacement

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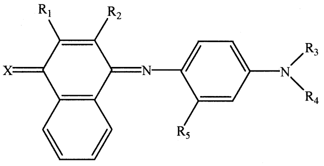
of the carbonyl group in compound **1a** by the more powerful dicyano vinyl acceptor group gave the naphthoquinone methide dyes **1c**, whose absorption maxima were shifted to longer wavelengths than compound **1a** [2]. A strong intramolecular charge transfer character was confirmed by PPP semi-expirical calculations. In the case of the naphthoquinone methide dyes, Yoshida et al. have also reported the single crystal structure of 4-(2′-acetylamino-4′-diethylamino)-1,4-dihydronaphthylidenemalononitrile (**1d**) [3].



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	X	R_1	R_2	R_3	R_4	R_5	λ_{max} (nm)
1a	O	H	H	CH_3	CH_3	H	583[a]
1b	O	CN	CN	CH_3	CH_3	H	795[a]
1c	$C(CN)_2$	H	H	C_2H_5	C_2H_5	H	711[b]
1d	$C(CN)_2$	H	H	C_2H_5	C_2H_5	NHAc	756[b]

[a] In trichloromethane.
[b] In benzene.

In an earlier study, we have reported the synthesis and metal complexation properties of a fluorescent squarylium dye containing a monoazacrown moiety [4]. As a continuation of this work, we now report the synthesis and crystal structure of the monoazacrown indoaniline dye **9**.

2. Experimental

Melting points were determined using an Electrothermal IA 900 and are uncorrected. Visible spectra were recorded on a Shimadzu UV-2100 spectrophotometer and CHN analyses were carried out using a Carlo Elba model 1106 analyzer. Mass spectra were recorded using a Shimadzu QP-1000 spectrometer with an electron energy of 70 eV and direct sample introduction. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Unity Inova 300 MHz FT-NMR spectrometer using TMS as internal standard. IR spectra were recorded with a Nicolet Magna-IR 500 spectrophotometer. Geometry optimization of the structure of dye **9** was carried out using MM2 followed by a AM1 level approximation on MOPAC by the Chem 3D system (Cambridge Soft Corp.).

2.1. 2-1 Synthesis of intermediates (**3**–**7**) *and azacrown indoaniline dye* (**9**)

2.1.1. 1,11-Dicholoro-3,6,9-trioxaundecane (**3**)

In a modification of the procedure of Martin et al. [5], tetraethylene glycol (150 g, 0.77 mol) in 40 cm^3 benzene was treated with thionyl chloride (195 g, 1.64 mol) and pyridine (135 g, 1.71 mol) at room temperature. After 24 h, the insoluble pyridinium salt was removed by filtration and the filtrate poured into 1 l of absolute ethanol. The resulting brown solution was heated for 3–4 h, during which time a copious evolution of gases occurred. The ensuing compound was concentrated in vacuo and the residue dissolved in ethyl acetate (800 cm^3). The resulting solution was washed with water and the ethyl acetate layer was dried with $MgSO_4$ and concentrated in vacuo. Distillation of the residue gave the dichloride as a pale yellow oil, b.p. 107–109°C/0.1 mm Hg. Yield 79%; single spot on TLC; IR (neat) no ν_{OH}; NMR ($CDCl_3$) δ 3.61–3.69 (m, 12H), 3.74–3.78 (m, 4H).

2.1.2. 1,11-Diiodo-3,6,9-trioxaundecane (**4**)

Powdered sodium iodide (160 g, 1.07 mol) was added to solution of 1,11-dichloro-3,6,9-trioxaundecane (**3**) (103.2 g, 0.45 mol) in acetone (260 cm^3), and the stirred mixture heated under reflux for 70 h. After cooling, the reaction mixture was filtered and the filtrate concentrated in vacuo, diluted with ethyl acetate (200 cm^3) and extracted with 20% sodium thiosulfate solution (200 cm^3). The organic layer was washed with water and dried ($MgSO_4$) and then was used directly in the following preparation. Removal of the solvent in vacuo gave the diiodide (**4**) (166 g) as a pale yellow oil. Yield: 90%. ^{1}H NMR ($CDCl_3$): δ 3.26 (t, 4H) 3.67 (s, 8H) 3.76 (t, 4H).

2.1.3. 10-Phenyl-1,4,7-trioxa-10-azacyclododecane (**6**)

A stirred solution of (**4**) (24.84 g, 0.0 6 mol) and aniline (5.6 g, 0.06 mol) in dry acetonitrile (800 cm^3) containing suspended powdered anhydrous sodium carbonate (21.3 g) was heated under reflux for 5 days. The cooled solution was filtered and the filtrate concentrated in vacuo; the residue was dissolved in chloroform (500 cm^3) and washed several times with water. The ensuing solution obtained was evaporated to dryness and submitted to column chromatography on silicagel using hexane:ethyl acetate (3:1/v:v). After removal of the solvent, the residue was distilled in vacuo to give the pure azacrown (**6**) as a colorless oil, b.p. 140–142°C/0.05 mm Hg. Yield: 27%. ^{1}H NMR (CDCl$_3$) δ 3.55 (t, 4H), 3.63 (m, 8H), 3.83 (t, 4H), 6.64–6.73 (m, 3H), 7.18 (t, 2H).

Table 1
Crystallographic data and intensity collection for dye **9**

Empirical formula	$O_4N_2C_{24}H_{26}$
Formula mass	406.48
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Z	4
a (Å)	8.970 (1)
b (Å)	14.597 (2)
c (Å)	16.189 (2)
β (°)	100.421 (5)
V (Å^3)	2084.8 (5)
D_{calc} (g/cm^3)	1.294
μ (cm^{-1} with Mo-K_α)	0.8
Transmission factor (%)	83.7134–99.8418
Scan type	ω–2θ
Scan width (ω) (°)	$0.98 + 0.55 \tan(\theta)$
$2\theta_{max}$ (°)	52.64
No. of reflections measured	1748
No. of reflections observed [$I > 3\sigma(I)$]	1139
No. of variables	349
R[a]	0.0448
R_w[b]	0.0491
Goodness of fit[c]	1.40
Maximum shift in final cycles	< 0.01

[a] $R = \sum |F_o - |F_c|| / \sum F_o$.

[b] $R_w \left| = \sum w(F_o - |F_c|)^2 / \sum wF_o \right|^{1/2}$, where $w = \sigma(F_2)^{-1}$.

[c] Estimated standard deviation of an observation of unit mass: $\sum w\ (F_o - F_c)^2/(N_o - N_v)^{1/2}$, where N_o = number of observations and N_v = number of variables.

2.1.4. 10-(4′-Nitrosophenyl)-1,4,7)-trioxa-10-azacyclododecane (**7**)

Compound (**6**) (5 g, 0.02 mol) was dissolved in concentrated hydrochloric acid (8.4 cm^3); crushed ice was added to this solution until the temperature fell below 5°C. Sodium nitrite (1.45 g, 0.021 mol) in water (3 cm^3) was slowly added and stirring continued for a further 2 h. The resulting aqueous solution was neutralized with 10% aqueous sodium hydroxide solution and extracted with chloroform. The chloroform solution was evaporated and column chromatographed on silicagel (ethyl acetate:hexane = 2:1/v:v) performed. The resulting green solid was recrystallized from

Table 2
Final atomic coordinates and thermal parameters for dye **9**

Atom[a]	x	y	z	B(A2)
O1	0.0690(5)	0.3455(4)	0.6937(3)	8.4(1)
O2	0.1916(4)	0.5749(2)	0.0519(2)	4.63(9)
O3	0.4974(4)	0.6591(3)	0.1087(2)	4.7(1)
O4	0.5772(4)	0.4786(2)	0.1647(2)	3.67(8)
N1	−0.0861(4)	0.3836(3)	0.3567(2)	4.0(1)
N2	0.2842(4)	0.3822(3)	0.1127(2)	3.4(1)
C1	0.0341(7)	0.3614(4)	0.6185(4)	5.6(2)
C2	−0.1251(6)	0.3658(4)	0.5765(3)	4.6(2)
C3	−0.2413(7)	0.3607(5)	0.6226(3)	6.3(2)
C4	−0.3862(7)	0.3653(5)	0.5851(4)	7.8(2)
C5	−0.4242(6)	0.3762(5)	0.5007(4)	7.1(2)
C6	−0.3166(6)	0.3802(4)	0.4536(3)	4.5(1)
C7	−0.1636(6)	0.3743(3)	0.4892(3)	3.6(1)
C8	−0.0436(5)	0.3810(4)	0.4374(3)	3.7(1)
C9	0.1089(6)	0.3889(4)	0.4833(3)	5.0(2)
C10	0.1433(6)	0.3798(5)	0.5662(4)	6.4(2)
C11	0.0140(5)	0.3812(4)	0.3000(3)	3.7(1)
C12	−0.0263(5)	0.4301(4)	0.2260(3)	4.1(1)
C13	0.0628(6)	0.4327(4)	0.1662(3)	3.6(1)
C14	0.1961(5)	0.3810(4)	0.1734(3)	3.2(1)
C15	0.2370(5)	0.3287(4)	0.2467(3)	3.7(1)
C16	0.1456(6)	0.3296(4)	0.3081(3)	3.7(1)
C17	0.2297(5)	0.4196(4)	0.0291(3)	4.0(1)
C18	0.2741(6)	0.5126(4)	0.0120(3)	4.0(1)
C19	0.2369(6)	0.6661(4)	0.0456(4)	5.7(2)
C20	0.3558(7)	0.6972(4)	0.1158(4)	5.9(2)
C21	0.5868(7)	0.6362(4)	0.1863(4)	5.8(2)
C22	0.5493(6)	0.5460(4)	0.2188(3)	5.1(2)
C23	0.5471(6)	0.3899(4)	0.1922(3)	4.4(1)
C24	0.4323(6)	0.3411(4)	0.1277(3)	3.9(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)* [$a2{*}B(1,1) + b2{*}B(2,2) + c2{*}B(3,3)ab$(cos gamma)*$B(1,2) + ac$ (cos beta)*(1,3) + bc(cos alpha)*$B(2,3)$].

benzene to afford 2.87 g of (**7**). Yield: 50%; m.p. 92–93°C; ^{1}H NMR (CDCl$_3$) δ 3.65 (m, 12H), 3.90 (t, 4H), 6.70 (d, 1H), 6.81 (d, 2H), 6.98 (d, 2H), 7.50 (d, 1H), 7.62 (t, 1H), 7.70 (t, 1H), 8.17 (d, 1H), 8.51 (d, 1H).

2.1.5. Azacrown indoaniline dye (**9**)

To a mixture of (**7**) (1.83 g, 6.5 mmol) with zinc powder (3 g) in aqueous hydrochloric acid (30 cm^3), an aqueous solution (35 cm^3) of α-naphthol (**8**) (0.94 g, 6.5 mmol) and sodium hydroxide (0.67 g) were added at room temperature and the mixture then stirred for 24 h using air oxidation. The product was filtered, washed with water, dried and then separated using column chromatography (ethyl acetate:hexane = 2:1/v:v). The isolated product was purified by recrystallization from ethyl acetate. Yield : 47%; m.p. 131°C. 1H NMR (CDCl$_3$) δ 3.65 (m, 12H), 3.90 (t, 4H), 6.70 (d, 1H), 6.81 (d, 2H), 6.98 (d, 2H), 7.50 (d, 1H), 7.62 (t, 1H), 7.70 (t, 1H), 8.17 (d, 1H), 8.51 (d, 1H). EA, calcd: C$_{24}$H$_{26}$N$_2$O$_4$ (C; 70.92, H; 6.45, N; 6.89), found: (C; 71.06, H; 6.51, N; 7.46); m/z (M$^+$); 406; ν cm^{-1} (KBr): 2861, 1652, 1123.

2.2. X-ray crystallographic analysis

Preliminary experiments and data collection for the X-ray crystal structure determination were performed on an Enraf–Nonius CAD 4/Turbo diffractometer using Mo-K_α radiation ($\lambda = 0.71069$ Å). A small single crystal, (0.5×0.5×0.5 mm), was cut from a larger one and was glued to a glass fiber using epoxy resin. Twenty-five reflections taken in diverse reciprocal space were centered using an automatic search program, and were used to obtain cell parameter. After the preliminary cell has been confirmed, high-angle data ($2\theta > 20°$) were collected and 25 of these reflections were centered and used to obtain more accurate cell parameters. Unit cell parameters and systematic absences indicated a monoclinic space group $P2_1$/c (No. 14) [6] with $Z = 4$. Data were collected on this improved unit cell at ambient temperature up to $2\theta = 52.64°$. Data reduction, including the correlation for Lorentz-polarization, decay, and absorption, were performed. Crystal structure was resolved and refined using full-matrix, least-square procedure using the Enraf–Nonius structure determination package, which resulted in final R_1 and R_W indices of 0.0448 and 0.0491, respectively.

The crystallographic data are summarized in Table 1 and the final structural parameters are presented in Table 2. The selected bond distances and bond angles are tabulated in Tables 3 and 4, respectively. The structure model was drawn using ORTEP, an Oak Ridge Thermal Ellipsoid Plot program and is shown in Fig. 1 [7].

3. Results and discussion

The crown ethers are macrocyclic, polyether crown compounds which generally, but not always, comprise oxygen, nitrogen and/or sulfur heteroatoms separated by two carbon atoms or their equivalent. Replacement of oxygen by sulfur, nitrogen and other heteroatoms has been explored extensively and has led to azacrown ethers, thiocrown ethers and other derivatives. Azacrowns are the simplest variants of the macrocyclic polyethers. A number of azacrown compounds were reported by Lockhart and her co-workers [8]. Synthesis of intermediates **3**, **4** and **6** was carried out using the method described previously [5]. Heating of the diiodide (**4**), the crude product

Table 3
Bond length (Å) for dye **9** with e.s.d. values given in parentheses

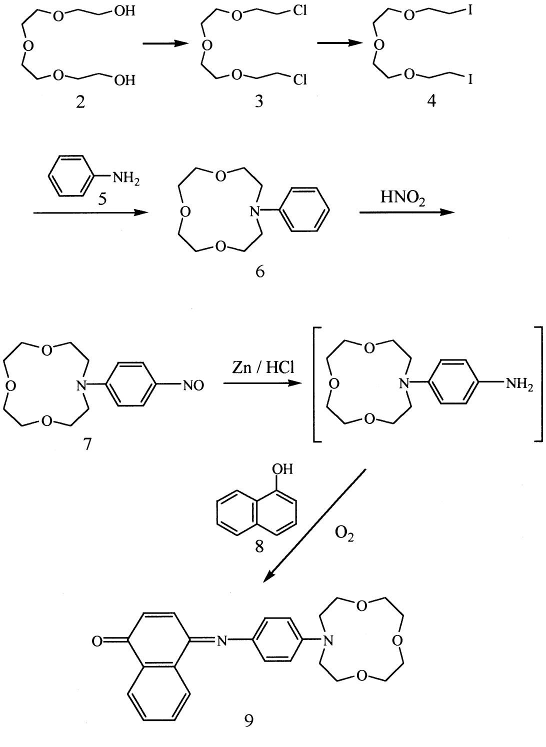
O1–C1	1.225(8)	C4–C5	1.36(1)
O2–C18	1.401(8)	C5–C6	1.335(9)
O2–C19	1.402(9)	C6–C7	1.391(8)
O3–C20	1.411(9)	C7–C8	1.483(8)
O3–C21	1.403(9)	C8–C9	1.439(8)
O4–C22	1.371(9)	C9–C10	1.33(1)
O4–C23	1.411(8)	C11–C12	1.386(8)
N1–C8	1.293(7)	C11–C16	1.386(8)
N1–C11	1.396(7)	C12–C13	1.363(8)
N2–C14	1.367(7)	C13–C14	1.400(8)
N2–C17	1.446(8)	C14–C15	1.400(8)
N2–C24	1.438(8)	C15–C16	1.359(9)
C1–C2	1.467(9)	C17–C18	1.49(1)
C1–C10	1.43(1)	C19–C20	1.48(1)
C2–C3	1.389(9)	C21–C22	1.48(1)
C2–C7	1.399(8)	C23–C24	1.51(1)
C3–C4	1.33(1)		

prepared from the dichloride (**3**) aniline in dilute acetonitrile solution containing dispersed Na_2CO_3 resulted in complete consumption of the dihalide and the formation of 10-phenyl-1,4,7-trioxa-10-azacyclododecane (**6**). Structural assignments were based on ^1H NMR and IR data.

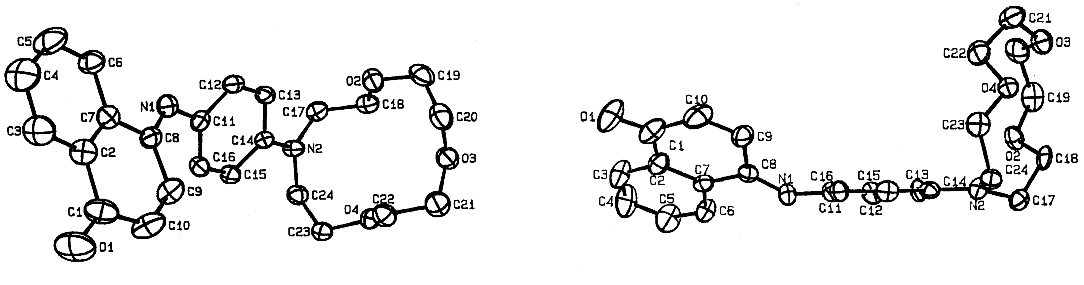
The nitrosonium ion, generated in situ from sodium nitrate in the presence of hydrochloric acid at 0–5°C, is a weak electrophile. Its attack of the aza-crown benzene ring leads to the 10-(4′-nitrosophenyl)-1,4,7-trioxa-10-azacyclo-dodecane (**7**) (50% yield). The azacrown indoaniline dye (**9**) was synthesized by condensing the nitroso compound (**7**) with α-naphthol (**8**) in alkaline solution, at room temperature, by air oxidation (Scheme 1). The indoaniline dye (**9**) showed a striking selectivity for Li^+ complexation, this being the subject of a subsequent publication. The indoaniline dye crystals were monoclinic and belonged to the $P2_1/c$ space group. Dye (**9**) is blue in colour and has an intense absorption band at 590 nm (ε_{max}. 13 550 l mol^{-1} cm^{-1}) in $CHCl_3$ solution. The structure of

Table 4
Bond angles (degrees) for dye **9**

C18–O2–C19	113.5(6)	N1–C8–C9	126.8(6)
C20–O3–C21	113.4(6)	C7–C8–C9	115.6(6)
C22–O4–C23	112.9(6)	C8–C9–C10	122.7(7)
C8–N1–C11	123.9(6)	C1–C10–C9	123.9(8)
C14–N2–C17	122.4(5)	N1–C11–C12	117.3(6)
C17–N2–C24	116.7(5)	C12–C11–C16	116.6(6)
C2–C1–C10	115.5(7)	N1–C11–C16	126.0(7)
O1–C1–C2	121.5(8)	C11–C12–C13	122.3(7)
C1–C2–C3	120.6(8)	C12–C13–C14	121.8(6)
C1–C2–C7	120.9(7)	N2–C14–C13	121.9(6)
C3–C2–C7	118.4(7)	N2–C14–C15	123.3(6)
C3–C4–C5	120.8(8)	C13–C14–C15	114.8(6)
C2–C3–C4	121.1(8)	C14–C15–C16	123.3(6)
C4–C5–C6	120.3(8)	N2–C17–C18	116.4(6)
C5–C6–C7	121.4(7)	O2–C18–C17	110.0(6)
C2–C7–C6	118.0(6)	O2–C19–C20	114.3(7)
C2–C7–C8	120.4(6)	O3–C20–C19	110.4(7)
C6–C7–C8	121.5(6)	O3–C21–C22	113.6(7)
N1–C8–C7	117.5(6)	O4–C22–C21	109.4(7)
N2–C24–C23	114.4(6)	O4–C23–C24	111.1(6)



Scheme 1.



(a) top view

(b) side view

Fig. 1. ORTEP view of molecular structure of dye **9** with thermal ellipsoids drawn at 50% probability level.

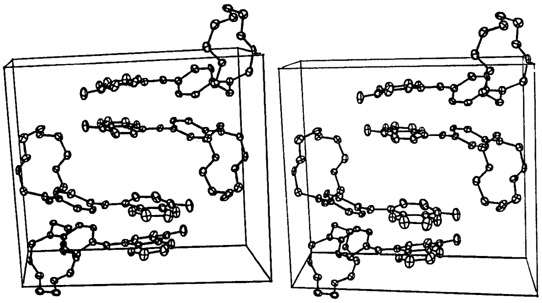


Fig. 2. Stereoview of crystal structure of dye **9**.

Table 5
Experimental and calculated angles (in degrees) for indoaniline dye **9**

	Obsd (°)[a]	Calcd (°)[b]
Plane I[c] and aniline ring	36.53	37.2
Plane I and C1–C2–C10	6.26	5
Plane I and C7–C8–C9	4.54	6.6
Plane I and C2–C3–C6–C7	5.15	4.4

[a] By X-ray study.

[b] Optimized by AM1 method.

[c] A plane C2–C7–C9–C10.

dye (**9**) was determined by X-ray analysis (Fig. 1), final R factors being $R_1 = 0.0448$ and $R_W = 0.0491$; the azacrown ring was almost vertical above the aniline ring [Fig. 2(a)]. Thus, the indoaniline dye was found to be non-planar, with a dihedral angle of 36.53° between the quinonimine and aniline benzene rings. The lack of planarity is probably due to the mutual steric crowding by the two hydrogens attached to C(9) and C(16). The ring formed by C(2)–C(7) is almost planar and is tilted from the plane of C(2)–C(7)–C(9)–C(10) (plane I) by 5.15°. The planes C(1)–C(2)–C(10) and C(7)–C(8)–C(9) were tilted from plane I by 6.26 and 4.54°, respectively. A stereo view of the crystal packing is shown in Fig. 2, from which it is apparent that two stereoisomers, of opposite rotational direction around the quinonimine ring, are disposed alternately. Each of the quinonimine rings lies approximately parallel with the *C*-axis, while each monoazacrown moiety is more widely separated in opposite direction. These results are in agreement with semi-empirical molecular orbital calculation (Table 5). Geometry optimization was carried out using MM2 (molecular mechanics) followed by an AM1 level approximation on MOPAC.

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