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Synthesis and characterization of 9-(4-nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridinedione and its methoxyphenyl derivative

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9-(4-Nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridinedione (NTHA) crystallizes in orthorhombic space group $P2_12_12_1$ with $a = 5.9716(1)$ Å, $b = 18.0476(3)$ Å, $c = 19.2445(2)$ Å, $V = 2074.04(5)$ Å^3, $Z = 4$, $D_{\mathrm{cal}} = 1.263$ Mg m^{-3} and $R = 0.0521$ ($wR = 0.1326$) for 4078 observed reflections. 9-(4-Nitrophenyl)-10-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridinedione NMTHA, crystallizes in monoclinic space group $P2_1/c$ with $a = 15.669(5)$ Å, $b = 10.652(4)$ Å, $c = 18.337(6)$ Å, $\beta = 108.25(1)^\circ$, $V = 2906.66(2)$ Å^3, $Z = 4$, $D_{\mathrm{cal}} = 1.245$ Mg m^{-3} and $R = 0.0725$ ($wR = 0.1847$) for 5105 observed reflections. The experimental values are compared with the theoretical values calculated based on the semiemperical methods. The structures are stabilized by N—H···O and C—H···O types of intermolecular interactions in addition to van der Waals forces.

KEY WORDS: Crystal structure; conformation; semiempirical; hydrogen bondings; acridinediones.

Introduction

The synthesis of 1,8-acridinediones has attracted the chemists for quite sometime owing to its pharmacological activities on this family of compounds. These acridinediones are found to possess a wide spectrum of biological properties such as anti-tumour,[1] antibacterial,[2] antiamoebic,[3] hypertensive and anti-inflammatory.[4]

The interactions of acridinediones with nucleic acids[5–8] are generally acknowledged to be responsible for their activities in part. The intercalation hypothesis[9] suggests that the planar aromatic ring system of the acridinediones become inserted (intercalated) in between two adjacent base pairs of a double-stranded nucleic acid.

In view of the above importance, the compounds 9-(4-nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridindione (NTHA) and its 10-methoxy phenyl derivative (NMTHA) are prepared and characterized by different methods.

The structural properties of these 1,8-acridinediones, namely NTHA and NMTHA are also studied by semiempirical (AM1, PM3) methods. The theoretically calculated values are compared with those derived from X-ray diffraction methods.

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This comparative study enables one to evaluate the validity of the theoretical methods to predict the geometrical features of acridinedione systems and apply to different activity studies.

Experimental

General

The IR spectra were measured with Shimadzu FTIR 8300 instrument as potassium bromide pellets. The ^{1}H and ^{13}C NMR spectra were recorded on Jeol-GSX400 (400 MHz) and DPX 200 (200 MHz) instruments. Mass spectra were obtained with Jeol-JMS-DX-303 HF.

Semiempirical calculations (AM1 and PM3) were carried out using the MOPAC 6.0 molecular orbitals set.

X-ray crystal structure

Crystals of NTHA and NMTHA were grown by slow evaporation method from ethanol solution at room temperature. Well-shaped crystals were chosen for X-ray diffractometric measurements on a Siemens SMART CCD[10] area detector with graphite monochromated MoKα radiation. The entire data collection was covered over a hemisphere of reciprocal space by a combination of three sets of exposures each having a different ϕ angle (0, 88, and 180°) for the crystal and each exposure time of 10 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was $-35°$. Crystal decay was monitored by repeating thirty initial frames at the end of the data collection and analyzing the duplicate reflections, and was found to be negligible.

Structure solutions were carried out by direct methods for both the compounds using SHELXS97[11] and refined by SHELXL97.[12] The solvent molecule ethanol appeared at the adjacent site of the nitrogroup. Hydrogen atoms were placed at the calculated positions but not refined. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The geometrical parameters were calculated by PARST[13] and the molecular graphics were drawn using ZORTEP.[14]

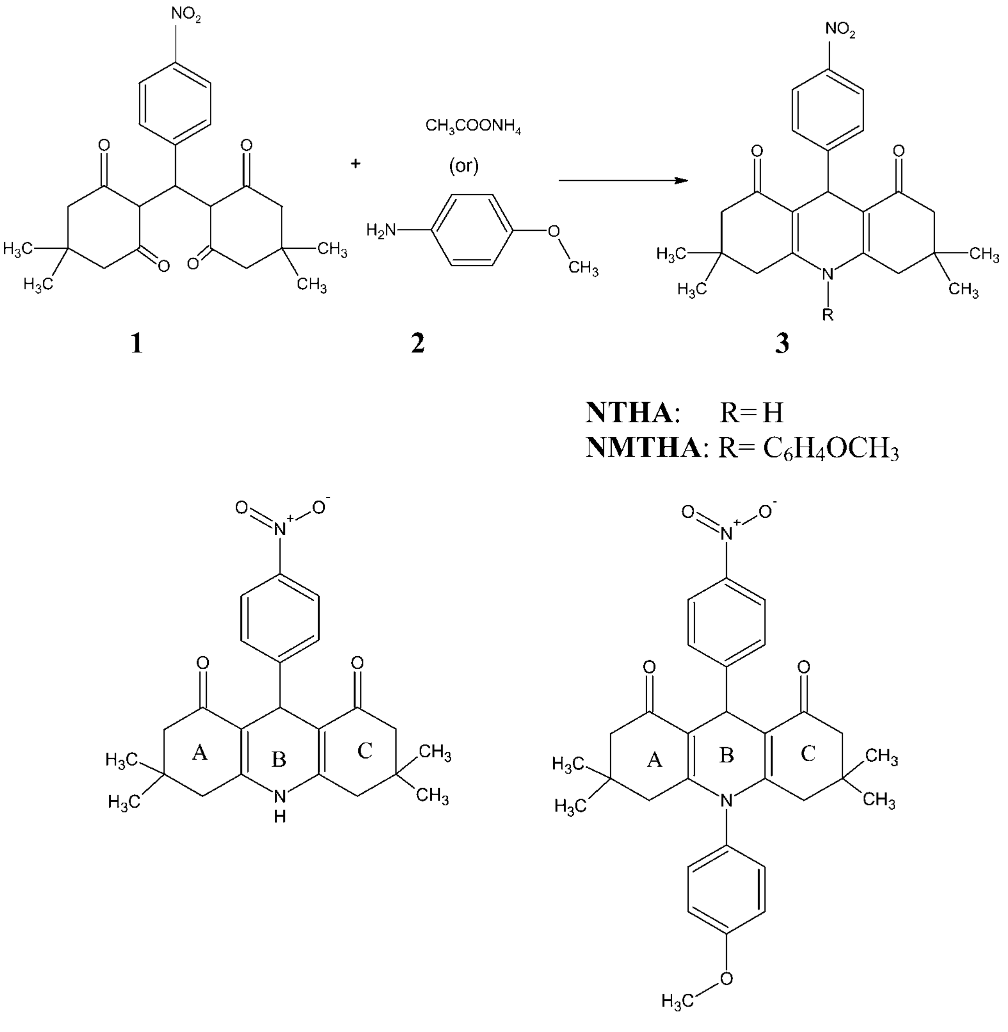
Synthesis

NTHA. A mixture of 2,2′-(4-nitrobenzylidene) bis (5,5-dimethylcyclohexane-1,3-dione) (1 g, 2.4 mmol) and ammonium acetate (3 g, 39 mmol) in acetic acid (20 ml) was refluxed for 6 h. The reaction mixture was cooled, poured into ice and the separated solid was filtered and recrystallized from a mixture a chloroform-methanol (5:1).

NMTHA. A mixture of 2,2′-(4-nitrobenzylidene) bis (5,5-dimethylcyclohexane-1,3-dione) (1 g, 2.4 mmol) and p-anisidine (0.3 g, 2.4 mmol) in acetic acid (20 ml) was refluxed for 6 h. The mixture was cooled, poured into ice and the separated solid was filtered and recrystallized from chloroform.

9-(4-Nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridinedione (NTHA)

Yield 0.82 g (87%); mp 258–260°C, IR (KBr): 3433 (N—H), 1648 (C=O), 1486, 1367, 1229 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.93 & 1.08 (2s, 12H, gemdimethyl), 2.05–2.22 (ABq, 4H, $J = 16.11$ Hz, C_2—CH_2), 2.33–2.45 (ABq, 4H, $J = 17.09$ Hz, C_4—CH_2), 5.05 (s, 1H, C_9—H), 7.47–8.03 (2d, 4H, $J = 8.79$ Hz, Ar—H) and 9.12 (s, 1H, NH).^{13}C NMR (CDCl$_3$, 100 MHz): δ 25.93, 28.38, 31.34, 33.33, 39.55, 49.52, 110.34, 121.88, 127.91, 144.65, 148.76, 153.56, and 193.95. Mass *m*/*z* (%) 394 (M$^+$, 2), 393(1), 378(1), 365(1), 335(2), 272(2), 271(4), 256(trace), 236(trace), 194(100), 180(66), 152(10), 138(16), 112(22) and 83(9). Analysis calculated for $C_{23}H_{26}N_2O_4$ (394.46): C, 70.03; H, 6.59; N, 7.10; Found: C, 69.66; H, 6.84; N, 6.98.



1 2 3

NTHA: R=H
NMTHA: R= $C_6H_4OCH_3$

NTHA **NMTHA**

Scheme 1.

9-(4-Nitrophenyl)-10-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridinedione (NMTHA)

Yield 0.9 g (75%); mp 288–290 °C; IR(KBr): 1639 (C=O), 1575, 1508, 1377, 1226 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.77 & 0.93 (2s, 12H, gem dimethyl), 1.84–2.09 (ABq, 4H, $J = 17.4$ Hz, $C_4{-}CH_2$), 2.06–2.20 (Abq, 4H, $J = 16$ Hz, $C_2{-}CH_2$), 3.90 (s,3H, $-OCH_3$), 5.31 (s, 1H, $C_9{-}H$), 7.03–7.12 (ABq, 4H, $J =$ 8.4 Hz, Ar—H) and 7.56–8.10 (ABq, 4H, $J =$ 8.8 Hz, Ar—H).^{13}C NMR ($CDCl_3$, 50 MHz): δ 26.68, 29.61, 32.32, 33.58, 41.77, 50.00, 55.60, 113.41, 115.15, 123.39, 128.26, 128.79, 131.01, 146.01, 150.99, 153.66, 159.98, and 195.66. Mass *m*/*z* (%): 500 (M^+, 2), 499(trace), 472(2), 378(4), 236(2), 194(98), 180(100), 152(20), 138(30), 112(14) and 83(8). Analysis calculated for $C_{30}H_{32}N_2O_5$ (500.58) C, 71.97; H, 6.44; N, 5.59; found C, 71.82; H, 6.28; N, 5.46).

Table 1. Crystal Data

Parameters	NTHA	NMTHA
Empirical formula	$C_{23}H_{26}N_2O_4$	$C_{30}H_{32}N_2O_5\cdot CH_3CH_2OH$
CCDC No.	232064	232065
Formula weight	394.46	544.63
Temperature (K)	293(2)	293(2)
Wavelength (MoKα) (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions		
a (Å)	5.9716(1)	15.669(5)
b (Å)	18.0476(3)	10.652(4)
c (Å)	19.2445(2)	18.337(6)
β (°)		108.25(1)
Volume (Å^3)	2074.04(5)	2906.66(2)
Z	4	4
Calculated density (Mg m^{-3})	1.263	1.245
Absorption coefficient (mm^{-1})	0.087	0.086
$F(000)$	840	1160
Crystal size (mm)	0.48 × 0.46 × 0.22	0.38 × 0.26 × 0.22
θ-range for data collection (°)	1.50–26.00	2.00–26.00
Index ranges	$-7 \leq h \leq 7$	$-16 \leq h \leq 18$
	$-22 \leq k \leq 22$	$-12 \leq k \leq 12$
	$-17 \leq 1 \leq 23$	$-21 \leq 1 \leq 19$
Reflections collected	12891	15871
Independent reflections	4078 [$R_{\text{int}} = 0.0836$]	5105 [$R_{\text{int}} = 0.0925$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4078/0/268	5105/0/355
Goodness-of-fit on F^2	0.959	0.989
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0521$, $wR_2 = 0.1326$	$R_1 = 0.0725$, $wR_2 = 0.1847$
R indices (all data)	$R_1 = 0.0667$, $wR_2 = 0.1413$	$R_1 = 0.1455$, $wR_2 = 0.2157$
Largest diff. peak and hole (e Å^{-3})	0.264 and −0.310	0.454 and −0.371

Results and discussion

9-(4-Nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridinedione and 9-(4-nitrophenyl)-10-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H, 5H) acridinedione were synthesized by the reaction of 2,2′-(4-nitrobenzylidene)bis(5,5-dimethyl cyclohexane-1,3-dione) (**1**) with ammonium acetate and p-anisidine (**2**) respectively in refluxing acetic acid (Scheme 1).

The compounds were obtained as crystalline solids after recrystallization from chloroform:methanol (5:1) mixture and their structures were confirmed by spectroscopic and X-ray diffraction methods (Section 3 X-ray Crystal Structure).

The compound NTHA showed bonds in the IR spectrum corresponding to the N—H (3433 cm^{-1}), C=O (1648 cm^{-1}) and —NO_2 (1846, 1367 cm^{-1}) groups. The ^{1}H-NMR spectrum of NTHA showed two singlets at δ 1.08 and 0.93 due to geminal dimethyl groups, an AB quartet between δ 2.05–2.22 with coupling constant $J_{\text{gem}} = 16.11$ Hz due to C_2—CH_2 protons, an another AB quartet between δ 2.33–2.45 with coupling constant $J_{\text{gem}} = 17.09$ Hz due to C_4—CH_2 protons, a singlet at δ 5.05 due to C_9 proton, two doublets between δ 7.47 and 8.03 with coupling constant $J = 8.79$ Hz due to aromatic protons and a singlet at δ 9.12 due to N—H proton.

The ^{13}C-NMR spectrum showed peaks at δ 25.93, 28.38, 31.34, 33.33, 39.55, 49.52, 110.34, 121.88, 127.91, 144.65, 148.76, 153.56, and

Table 2. Bond Lengths (Å), Bond Angles (°) and Torsion Angles (°) for NTHA

Bond	X-ray	AM1	PM3	Bond	X-Ray	AM1	PM3
Bond length (Å)							
C1—C2	1.515(3)	1.565	1.550	C7—C8	1.509(4)	1.561	1.539
C1—O16	1.225(3)	1.231	1.231	C8—C12	1.459(3)	1.231	1.539
C1—C13	1.463(3)	1.550	1.550	C8—O15	1.234(3)	1.231	1.231
C2—C3	1.528(3)	1.569	1.565	C9—C13	1.523(3)	1.561	1.561
C3—C26	1.532(3)	1.553	1.547	C9—C12	1.522(3)	1.561	1.561
C3—C27	1.527(3)	1.547	1.547	C9—C17	1.532(3)	1.563	1.563
C3—C4	1.542(3)	1.535	1.569	N10—C11	1.374(3)	1.456	1.362
C4—C14	1.485(3)	1.362	1.535	N10—C14	1.384(3)	1.456	1.456
C5—C6	1.519(3)	1.550	1.535	C11—C12	1.335(3)	1.362	1.362
C5—C11	1.498(3)	1.535	1.539	C13—C14	1.338(3)	1.362	1.362
C6—C7	1.532(4)	1.561	1.550	C20—N23	1.474(4)	1.505	1.505
C6—C28	1.529(4)	1.547	1.553	N23—O24	1.210(4)	1.221	1.221
C6—C29	1.533(3)	1.553	1.547	N23—O25	1.232(4)	1.221	1.221
Bond angles (°)							
O16—C1—C2	121.6(2)	119.49	119.49	C7—C6—C28	110.3(2)	109.69	11.53
C1—C2—C3	113.3(2)	114.39	114.39	C7—C8—O15	121.2(2)	119.49	119.49
C2—C3—C4	108.2(2)	109.84	109.85	C7—C6—C29	109.6(2)	109.16	109.15
C2—C3—C26	110.2(2)	109.16	109.15	C9—C17—C18	120.3(2)	121.96	119.14
C2—C3—C27	110.8(2)	110.53	110.52	C9—C17—C22	121.4(2)	119.14	121.96
C3—C4—C14	112.5(2)	115.15	115.18	C13—C9—C17	112.5(2)	111.11	111.10
C4—C14—N10	111.9(2)	117.69	117.69	C17—C22—C21	120.9(2)	120.54	120.53
C5—C11—C12	125.6(2)	122.65	122.66	C21—C20—N23	118.9(3)	120.68	120.64
C5—C6—C28	110.1(2)	110.54	109.96	C20—N23—O24	119.1(3)	121.18	121.18
C6—C7—C8	115.1(2)	114.41	114.39	C20—N23—O25	118.5(3)	121.18	121.18
C7—C8—C12	117.6(2)	118.58	118.57				
Torsion angles (°)							
O16—C1—C2—C3	−36.8(3)	−40.46	44.35	C9—C12—C8—C7	−177.6(2)	174.02	−173.84
C1—C2—C3—C4	55.7(3)	46.75	−46.31	C13—C9—C12—C8	−156.2(2)	164.87	−165.02
C1—C2—C3—C26	−63.8(3)	−75.47	75.43	C9—C12—C11—C5	177.4(2)	−174.48	174.46
C1—C2—C3—C27	175.4(2)	166.69	−166.73	C12—C9—C13—C14	−22.7(3)	14.90	−14.77
C2—C3—C4—C14	−45.3(8)	−46.40	46.31	C3—C4—C14—N10	−164.09(8)	−154.09	154.25
C3—C4—C14—C13	17.2(3)	27.22	−27.10	C4—C14—C13—C9	−175.9(1)	174.48	−174.46
C12—C8—C7—C6	−30.0(2)	28.04	−28.01	C21—C20—N23—O24	4.1(5)	0.00	0.00
C8—C7—C6—C28	−67.3(2)	75.47	−75.43	C21—C20—N23—O25	−173.6(3)	−179.99	−179.99
C8—C7—C6—C29	171.8(2)	−166.69	166.73				

193.95 (C=O). Mass spectrum shows a peak at *m*/*z* 394 corresponding to the molecular ion. The elemental analysis was concurrent with the theoretical value. Similarly, the spectral and analytical data for the compound NMTHA were consistent with the expected structure.

The crystallographic data for the compounds NTHA and NMTHA are presented in Table 1. The bond lengths, bond angles and torsion angles derived from X-ray diffraction methods and calculated based on semiemprical methods for NTHA and NMTHA for comparison are given in Tables 2 and 3. A study of the results shows that the theoretically calculated values are in good agreement with the experimental observation.

The ZORTEP plots of the molecules NTHA and NMTHA are shown in Fig. 1a and b. The central pyridine ring B of acridinedione moiety tends to be planar, which is evident from the π-conjugation along the bonds C12—C11—N10—C14—C13 in both the molecules NTHA and NMTHA. This is evident from the conformation angles and bond lengths around the ring B as detailed below:

Table 3. Bond Lengths (Å), Bond Angles (°) and Torsion Angles (°) for NMTHA

Bond	X-Ray	AM1	PM3	Bond	X-Ray	AM1	PM3
Bond length (Å)							
C1−C2	1.506(5)	1.546	1.503	C8−C12	1.466(5)	1.544	1.518
C1−O16	1.237(4)	1.231	1.220	C8−O15	1.231(4)	1.232	1.220
C2−C3	1.531(5)	1.566	1.527	C9−C12	1.513(5)	1.551	1.523
C3−C4	1.542(5)	1.566	1.528	C9−C13	1.507(4)	1.551	1.524
C3−C26	1.530(5)	1.547	1.547	C9−C17	1.527(4)	1.565	1.537
C3−C27	1.518(5)	1.553	1.544	N10−C11	1.410(4)	1.501	1.469
C4−C14	1.505(4)	1.554	1.537	C11−C12	1.344(4)	1.364	1.366
C5−C6	1.522(5)	1.555	1.537	C13−C14	1.346(4)	1.364	1.368
C6−C7	1.505(5)	1.546	1.504	C20−N23	1.464(5)	1.505	1.412
C6−C28	1.534(5)	1.553	1.544	N23−O24	1.244(4)	1.221	1.262
C6−C29	1.533(5)	1.547	1.547	N23−O25	1.233(4)	1.221	1.289
C7−C8	1.499(5)	1.546	1.504				
Bond angles (°)							
O16−C1−C2	120.8(4)	119.01	119.01	C9−C12−C8	117.2(3)	117.34	118.41
C1−C2−C3	114.8(2)	114.42	116.63	C9−C12−C11	122.8(3)	120.89	121.88
C2−C3−C4	107.1(3)	109.03	107.93	C9−C13−C14	122.7(3)	120.80	122.09
C2−C3−C26	110.8(3)	110.78	110.71	C9−C17−C18	121.5(3)	122.10	121.75
C2−C3−C27	110.1(3)	109.36	110.71	C12−C8−C7	117.9(3)	118.91	117.49
C3−C4−C14	113.2(3)	116.47	113.73	C13−C9−C12	109.2(3)	115.05	113.70
C4−C14−N10	115.9(3)	120.75	117.74	C13−C9−C17	111.8(3)	110.77	111.81
C4−C14−C13	123.0(3)	119.58	120.79	C17−C18−C19	121.7(3)	120.52	121.18
C5−C11−C12	122.6(3)	119.47	121.19	C18−C19−C20	118.1(3)	120.65	117.94
C6−C7−C8	112.8(3)	114.44	116.85	C19−C20−C21	122.3(3)	118.67	120.39
C7−C8−O15	121.6(3)	118.94	119.56	C20−N23−O25	117.0(4)	121.19	118.15
C7−C6−C28	110.8(3)	109.32	110.77	C20−N23−O24	120.0(4)	121.17	121.09
C7−C6−C29	109.4(3)	110.78	108.93				
Torsion angles (°)							
C1−C2−C3−C4	−51.2(4)	46.55	−49.41	C14−N10−C30−C31	−98.6(4)	104.50	−104.02
C1−C2−C3−C26	68.7(4)	−75.51	72.10	C9−C12−C8−C7	−178.4(3)	−174.94	169.69
C1−C2−C3−C27	−169.9(3)	166.28	−166.22	C9−C12−C11−C5	−174.7(3)	176.68	−174.94
C2−C3−C4−C14	50.3(4)	−48.99	52.59	C14−C13−C9−C12	21.1(4)	−19.17	1.78
C3−C4−C14−N10	157.6(3)	157.13	157.60	C4−C14−C13−C9	173.5(3)	−173.66	173.96
C3−C4−C14−C13	−22.1(5)	24.78	−27.22	C19−C20−N23−O24	6.3(5)	−0.000	−0.051
C12−C8−C7−C6	−33.9(5)	22.58	−18.54	C19−C20−N23−O25	−175.4(4)	−179.95	179.92
C13−C9−C12−C11	−20.5(4)	19.07	−1.06	C32−C33−O36−C37	2.5(5)	0.26	−2.32
C13−C9−C12−C8	159.7(3)	162.92	178.97	C34−C33−O36−C37	−177.1(3)	174.68	176.13

Atoms	NTHA	NMTHA
Conformation angles (°)		
C9−C12−C11−N10	−3.6(3)	6.1(5)
C12−C11−N10−C14	−16.8(3)	10.6(5)
C11−N10−C14−C13	15.8(3)	−10.1(4)
N10−C14−C13−C9	5.5(3)	−7.2(5)
Bond lengths (Å)		
C12−C11	1.335(3)	1.344(4)
C11−N10	1.374(3)	1.410(4)
N10−C14	1.384(3)	1.405(4)
C14−C13	1.338(3)	1.346(4)

The planarity of the pyridine ring B is further supported by the low value of the puckering amplitudes QT = 0.265(2) and 0.220(3)[15] when compared with the values of the other A and C rings for which QT = 0.466(2) and 0.455(2) for NTHA, and 0.482(4) and 0.478(4) for NMTHA, respectively.

In NTHA, the molecule contains a pseudo-mirror plane, which is passing through the atoms N10 and C9. A comparison of equivalent bond lengths and torsion angles across the

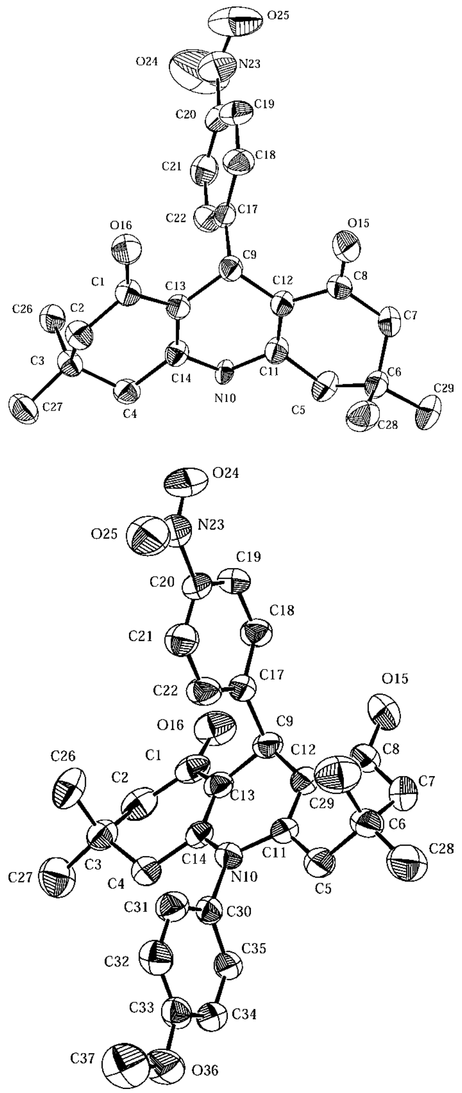


Fig. 1. (a) ZORTEP plot of the molecule NTHA with the thermal ellipsoids are drawn at 30% probability level. (b) ZORTEP plot of the molecule NMTHA with the thermal ellipsoids are drawn at 30% probability level.

pseudo-mirror plane indicates the presence of non-crystallographic symmetry element. The dihedral angle between the two mean planes passing through the group of atoms [C1/C2/C3/C4/C14/C13/C9/N10] and [C5/C6/C7/C8/C11/C12/C9/N10] is 24.3(1)° and this implies that the acridine moiety is slightly folded about a line passing through N10 and C9. A similar kind of situation was noted in related structures.[16,17] In NMTHA, the degree of folding was comparatively less and this is shown from dihedral angle value between the pseudo-mirror plane which is 10.2(1)°.

The planarity of the nitrogroup is due to the delocalization along the $\mathrm{N}\overset{\mathrm{O}}{\underset{\mathrm{O}}{<}}$ system. The bond distances [N23—O24 =] 1.210(4) Å; 1.224(4) Å and [N23—O25 =] 1.232(4) Å; 1.233(4) Å for NTHA and NMTHA agree with the reported average val-

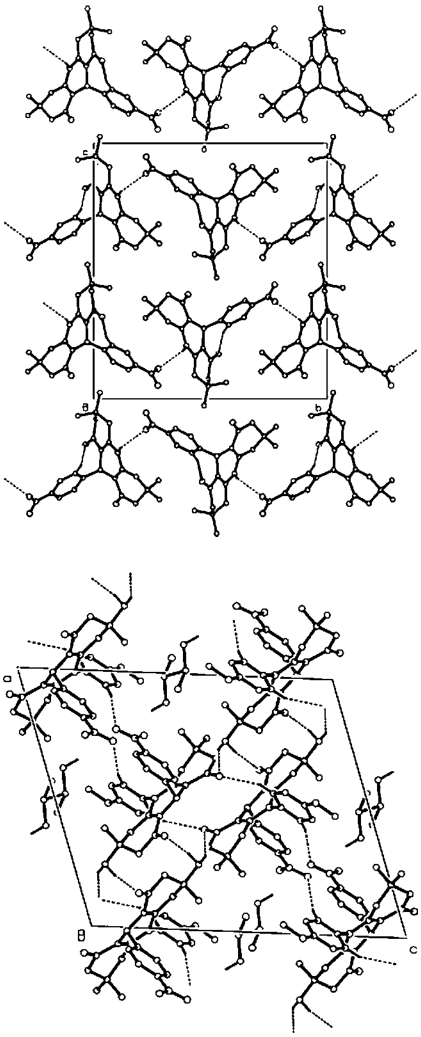


Fig. 2. (a) Packing of the molecules in NTHA viewed down the a-axis. (b) Packing of the molecules in NMTHA viewed down the b-axis.

Table 4. Hydrogen Bondings for NTHA [Å & (°)]

D—H	D···A	H···A	D—H···A	*Sym
N10—H10	N10···O24	H10···O24	N10—H10···O24	(1)
0.860(1)	3.257(3)	2.593(3)	134.8(1)	
C5—H5A	C5···O15	H5A···O15	C5—H5A···O15	(2)
0.970(2)	3.726(3)	2.765(2)	170.9(1)	
C22—H22	C22···O16	H22···O16	C22—H22···O16	(2)
0.930(2)	3.413(3)	2.531(1)	158.6(1)	
C5—H5B	C5···O24	H5B···O24	C5—H5B···O24	(1)
0.970(2)	3.806(4)	2.940(3)	149.1(1)	
C27—H27B	C27···O15	H27B···O15	C27—H27B···O15	(3)
0.960(2)	3.720(3)	2.821(2)	156.2(1)	

*Symmetry equivalent positions: (1) $-x+2, +y-1/2, -z+1/2$; (2) $x+1, +y, +z$; (3) $-x+1/2, -y+1, +z-1/2$.

ues of 1.215 and 1.225 Å.[18–20] The C—N bond lengths [C20—N23 =] 1.474(4) Å and 1.464(5) Å are comparable with many of the p-substituted nitrophenyl structures.[21–23] The keto bond lengths [C8—O15 =] 1.234(3); 1.231(4) Å; [C1—O16 =] 1.225(3); 1.237(4) Å for NTHA and NMTHA are in agreement with the values observed for similar structures.[24–26]

In NTHA and NMTHA, the nitro group shows a tendency to be coplanar with the phenyl ring. This can be seen from the following conformation angles:

Table 5. Hydrogen Bondings for NMTHA [Å & (°)]

D—H	D···A	H···A	D—H···A	*Sym
C4—H4A	C4···O24	H4A···O24	C4—H4A···O24	(1)
0.970(4)	3.678(5)	2.777(4)	154.8(2)	
C34—H34	C34···O15	H34···O15	C34—H34···O15	(1)
0.930(4)	3.590(5)	2.699(3)	160.8(2)	
C37—H37B	C37···O25	H37B···O25	C37—H37B···O25	(1)
0.960(2)	3.902(4)	2.971(3)	163.9(2)	
C31—H31	C31···O25	H31···O25	C31—H31···O25	(2)
0.930(4)	3.493(5)	2.591(3)	163.6(3)	
C21—H21	C21···O24	H21···O24	C21—H21···O24	(2)
0.930(5)	3.748(6)	2.900(4)	152.3(3)	
C22—H22	C22···O25	H22···O25	C22—H22···O25	(2)
0.930(4)	3.518(6)	2.801(4)	134.6(2)	
C35—H35	C35···O16	H35···O16	C35—H35···O16	(3)
0.930(4)	3.403(5)	2.529(3)	156.7(2)	
C27—H27C	C27···O15	H27C···O15	C27—H27C···O15	(3)
0.960(5)	3.814(6)	2.920(3)	155.4(3)	
C28—H28C	C28···O15	H28C···O15	C28—H28C···O15	(4)
0.960(5)	3.513(6)	2.582(3)	163.5(3)	
C38—H38B	C38···O25	H38B···O25	C38—H38B···O25	(5)
0.960(2)	3.643(4)	2.750(4)	155.3(2)	
C38—H38B	C38···N23	H38B···N23	C38—H38B···N23	(5)
0.960(2)	3.323(4)	2.563(3)	136.2(2)	

*Symmetry equivalent positions: (1) $x, +y-1, +z$; (2) $-x-1/2, +y-1/2, -z+1/2$; (3) $-x, -y+2, -z$; (4) $-x+1/2, +y-1/2, -z+1/2$; (5) $x+1, +y-1, +z$.

Atoms	NTHA	NMTHA
C19−C20−N23−O24	−176.5(4)°	6.3(5)°
C19−C20−N23−O25	5.8(4)°	−172.1(4)°
C21−C20−N23−O24	4.1(5)°	−175.4(4)°
C21−C20−N23−O25	−173.6(3)°	6.3(6)°

The nitrophenyl group is approximately perpendicular to the pyridine ring B (the subtending angles are 89.7(1)° for NTHA and 88.9(1)° for NMTHA) and this may be due to the steric hindrance between the keto oxygens.

In NTHA, the dimethyl groups attached to the rings A and C adopt axial and equatorial orientations, which is evident from the torsion angles [C26−C3−C4−C14] = 74.7(2)°, [C27−C3−C4−C14] = −166.0(2)°, [C11−C5−C6−C28] = 69.6(3)° and [C11−C5−C6−C29] = −169.6(2)°. In NMTHA, a similar situation exists for the dimethyl groups attached to the rings A and C. The torsion angles: [C26−C3−C4−C14] = −70.2(4)°, [C27−C3−C4−C14] = 169.5(3)°, [C11−C5−C6−C29] = 70.6(4)° and [C11−C5−C6−C28] = −169.6(3)° confirm the axial and equatorial orientations in this molecule also.

The packing of the molecules in the unit cell for NTHA and NMTHA are shown in Fig. 2a and b. In NTHA, the N−H group (N10−H10) forms hydrogen bonding with the nitro-oxygen substituted at C9-position. The details are: N10−H10 = 0.860(1) Å, N10−O24 $(-x+2, y-1/2, -z+1/2)$ = 3.257(3) Å, H10−O24 = 2.593(3) Å and an angle of N10−H10···O24 = 134.8(1)°. Interesting to note that this hydrogen bond plays a major role in exhibiting polymeric chains along b-direction. In NMTHA, the molecules in the unit cell are packed in a discrete fashion. However the atom C38 of the solvent molecule forms an interaction with the N23 atom of the nitrogroup. The keto oxygens O15 and O16 are also involved in C−H···O type of intermolecular interactions. The details of the hydrogen bondings are given in Tables 4 and 5.

Supplementary material NTHA: CCDC-232064 & NMTHA: CCDC-232065 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, United Kingdom; Fax: (+44) 1223-336-033: e-mail: deposit@ccdc.cam.ac.uk.

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