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著者	KUBO, Kanji
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Crystal Structure of 9,10-Bis(morpholinomethyl)anthracene

Kanji KUBO

Abstract

Structure of 9,10-Bis(morpholinomethyl)anthracene (**1**), $C_{24}H_{28}N_2O_2$, was determined by X-ray crystallographic analysis. The two morpholine rings are in an *anti* conformation with respect to one another across the anthracene ring. The crystal packing is consolidated by intermolecular C-H $\cdots\pi$ and C-H \cdots O interactions.

1. Introduction

As an approach to the manipulation of an intramolecular electron transfer dynamics, photo-responsive supramolecular systems are of great significance particularly for their potential application to nanoscale devices for cation sensor and switch.¹⁻³⁾ There are extensive investigations toward the characterization of photoinduced electron transfer (PET) fluoroionophores including ionophore with naphthalene, anthracene, pyrene, and coumarin fluorophore. Recently, it was found that the azacrown ethers act as electron donors in a typical exciplex-forming system that involves an appropriate electron acceptor. The addition of metal salts changed the fluorescence intensity of PET fluoroionophore. Moreover, the crystal structures of PET fluoroionophores such as 7,16-bis(1-naphthylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**Np186Np**),⁴⁾ its HNCS salt (**Np186Np**·2HNCS),⁵⁾ lithium thiocyanate complex (**Np186Np**·2LiNCS),⁶⁾ potassium thiocyanate complex (**Np186Np**·KNCS),⁷⁾ barium thiocyanate complex (**Np186Np**·Ba(NCS)₂·H₂O),⁷⁾ zinc thiocyanate complex ((H₂·**Np186Np**) [Zn(NCS)₄])⁶⁾, 7,16-bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, *N,N',N'',N'''*-tetrakis(1-naphthylmethyl)-1,4,8,11-tetraazacyclotetradecane,^{8,9)} *N,N'*-[9,10-anthracenediyl-bis(methylene)]bis[*N*-(2-ethoxyoxoethyl)]-glycine 1,1'-diethyl ester,¹⁰⁾ 1,4-bis(1-naphthylmethyl)piperazine,¹¹⁾ 1,4-bis(9-anthracenylmethyl)piperazine,¹²⁾ *N9,N9,N10,N10*-tetraethyl-9,10-anthracenedimethanamine,¹³⁾ *N,N,N',N'*-tetraethyl-9,10-anthracenedimethanamine dihydrogen tetrachlorozincate,¹⁴⁾ 1,1'-[9,10-anthracenediyl-bis(methylene)]bis[4-methylpiperazine],¹⁴⁾ 1,1'-[9,10-anthracenediylbis(methylene)]

* 北海学園大学工学部生命工学科

* Department of Life Science and Technology, Faculty of Engineering, Hokkai-Gakuen University

bis [4- (2-pyridinyl) piperazine] ,¹⁵⁾ *N* 9, *N* 9, *N* 10, *N* 10-tetrakis (2-pyridinylmethyl) -9,10-anthracenedimethanamine,¹⁴⁾ tetrachloro [μ - [*N,N,N',N'* - tetrakis [(2-pyridinyl- κ *N*) methyl] -9,10-anthracenediamine]] di-zinc,¹⁴⁾ and 9-(thiomorpholinomethyl)anthracene¹⁶⁾ were elucidated by X-ray crystallographic analysis. De Silva et al. have reported 9,10-bis(morpholinomethyl)anthracene (**1**) as a fluorescent pH indicator.¹⁷⁾ However the crystal structure of **1** has not been elucidated by X-ray analysis. We now report on the structure of 9,10-bis(morpholinomethyl)anthracene with the aim of contributing to a deeper understanding of PET systems.

2. Experimental

2.1. Material

9,10-Bis(morpholinomethyl)anthracene (**1**) was synthesized by the reaction of 9,10-di(chloromethyl)anthracene and morpholine in the triethylamine and toluene.¹⁸⁾ Single crystals of **1** for X-ray analysis were grown by slow evaporation of a chloroform solution at room temperature.

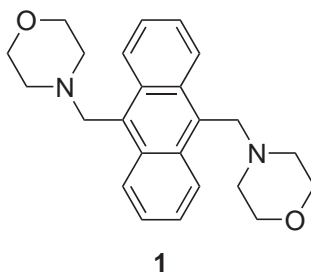


Fig. 1. Chemical structure of title compound (**1**).

2.2. Data Collection

A yellow prism crystal of $C_{24}H_{26}O_2N_2$ having approximate dimensions of $0.37 \times 0.25 \times 0.03$ mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-K α radiation. Indexing was performed from 3 oscillations that were exposed for 45 seconds. The crystal-to-detector distance was 127.40 mm. Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions : $a=8.883(3)$ Å, $b=9.149(3)$ Å, $c=24.371(7)$ Å, $V=1980.5(10)$ Å³. For $Z=4$ and $F.W. = 374.48$, the calculated density is 1.256 g/cm³. Based on the systematic absences of : $0kl : 1 \pm 2n$, $h0l : h \pm 2n$ packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $Pca2_1$. The data were collected at a temperature of $-100 \pm 1^\circ\text{C}$ to a maximum 2θ value of 136.5° . A total of 189 oscillation images were collected. A sweep of data was done using ω scans from 50.0 to 230.0° in 5.0° step, at c

=50.0° and $\phi = 0.0^\circ$. The exposure rate was 30.0 [sec./°]. A second sweep was performed using ω scans from 50.0 to 230.0° in 5.0° step, at $c=50.0^\circ$ and $\phi = 90.0^\circ$. The exposure rate was 30.0 [sec./°]. Another sweep was performed using ω scans from 50.0 to 230.0° in 5.0° step, at $\chi=50.0^\circ$ and $\phi = 180.0^\circ$. The exposure rate was 30.0 [sec./°]. Another sweep was performed using ω scans from 50.0 to 230.0° in 4.0° step, at $\chi=50.0^\circ$ and $\phi = 285.0^\circ$. The exposure rate was 30.0 [sec./°]. Another sweep was performed using ω scans from 50.0 to 230.0° in 5.0° step, at $\chi=10.0^\circ$ and $\phi = 60.0^\circ$. The exposure rate was 30.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

2.3. Data Reduction

Of the 20946 reflections that were collected, 3615 were unique ($R_{\text{int}}=0.059$); equivalent reflections were merged. The linear absorption coefficient, μ , for Cu-K α radiation is 6.327 cm⁻¹. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.729 to 0.981. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction¹⁹ was applied (coefficient = 0.001460).

2.4. Structure Solution and Refinement

The structure was solved by direct methods²⁰ and expanded using Fourier techniques.²¹ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 3615 observed reflections and 255 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0663$, $wR_2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} = 0.1600$. The standard deviation of an observation of unit weight was 1.08. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.20 and -0.25 e-/Å³, respectively. The absolute structure was deduced based on Flack parameter, 1.5(9), using 1750 Friedel pairs.²²

Neutral atom scattering factors were taken from Cromer and Waber.²³ Anomalous dispersion effects were included in F_{calc} ;²⁴ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.²⁵ The values for the mass attenuation coefficients are those of Creagh and Hubbell.²⁶ All calculations were performed using the *CrystalStructure*²⁷ crystallographic software package except for refinement, which was performed using *SHELXL97*.²⁸ Fractional atomic coordinates and equivalent isotropic displacement parameters were shown in **Table 1**. Anisotropic displacement parameters were shown in **Table 2**.

Table 1. Fractional atomic coordinates, equivalent isotropic displacement parameters ($B_{\text{iso}}/B_{\text{eq}}$)

atom	x	y	z	B_{eq}
O1	0.8177(6)	0.3448(5)	-0.1190(2)	7.59(16)
O2	0.1884(7)	0.1544(6)	0.3403(2)	8.3(2)
N1	0.6250(5)	0.2223(5)	-0.03628(17)	3.28(8)
N2	0.3692(5)	0.2800(5)	0.25702(18)	3.94(9)
C1	0.7923(6)	0.1201(5)	0.1070(2)	3.57(11)
C2	0.8833(7)	0.1246(6)	0.1505(2)	4.35(12)
C3	0.8336(7)	0.1875(6)	0.2020(2)	4.20(13)
C4	0.6952(6)	0.2450(6)	0.2037(2)	3.79(11)
C5	0.5952(5)	0.2499(5)	0.1578(2)	2.85(8)
C6	0.4522(6)	0.3180(5)	0.1616(2)	3.16(10)
C7	0.3584(5)	0.3178(5)	0.1154(2)	2.96(9)
C8	0.2089(6)	0.3807(6)	0.1168(2)	4.02(13)
C9	0.1173(7)	0.3790(7)	0.0710(3)	4.89(15)
C10	0.1679(7)	0.3160(6)	0.0235(2)	4.58(14)
C11	0.3073(5)	0.2535(6)	0.0184(2)	3.61(11)
C12	0.4067(6)	0.2510(5)	0.0645(2)	3.30(9)
C13	0.5496(6)	0.1854(5)	0.0616(2)	2.95(9)
C14	0.6459(6)	0.1839(5)	0.1076(2)	2.96(9)
C15	0.5965(6)	0.1130(5)	0.00695(19)	3.06(10)
C16	0.4092(7)	0.3880(6)	0.2147(2)	4.42(13)
C17	0.6532(9)	0.1486(6)	-0.0885(2)	5.85(18)
C18	0.6682(8)	0.2647(8)	-0.1323(2)	5.98(15)
C19	0.7910(8)	0.4127(6)	-0.0677(2)	4.91(14)
C20	0.7588(7)	0.3053(5)	-0.0226(2)	3.61(10)
C21	0.3547(10)	0.3543(7)	0.3105(2)	6.7(2)
C22	0.2927(13)	0.2385(9)	0.3524(3)	10.9(4)
C23	0.2036(7)	0.0831(7)	0.2886(2)	4.92(14)
C24	0.2339(7)	0.1947(7)	0.2443(2)	4.95(15)

$$B_{\text{eq}}=8/3\pi^2(U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}(aa^*bb^*)\cos \gamma+2U_{13}(aa^*cc^*)\cos \beta+2U_{23}(bb^*cc^*)\cos \alpha)$$

3. Result & Discussion

Compound (**1**) was prepared by the *N*-alkylation of morpholine of 9,10-di(chloromethyl)anthracene in the triethylamine and toluene. Single crystals of **1** for X-ray analysis were grown by slow evaporation of a chloroform solution. The crystal structure of **1** was shown in **Fig. 2**. A molecular view of **1** was shown in **Fig. 2**. The two morpholine rings are in an *anti* conformation with respect to one an-

Table 2. Anisotropic displacement parameters (\AA^2)

Atom	U ¹¹	U ²²	U ³³	U ¹²	U ¹³	U ²³
O1	0.141(5)	0.065(2)	0.083(3)	-0.043(2)	0.069(3)	-0.028(2)
O2	0.156(6)	0.091(4)	0.066(3)	0.074(3)	0.065(4)	0.045(3)
N1	0.051(2)	0.044(2)	0.030(2)	-0.020(2)	0.006(2)	-0.0067(19)
N2	0.069(3)	0.050(2)	0.031(2)	0.025(2)	0.010(2)	0.003(2)
C1	0.043(3)	0.049(3)	0.044(3)	0.003(2)	0.009(2)	-0.005(2)
C2	0.049(3)	0.053(3)	0.064(3)	0.008(2)	0.008(3)	-0.016(3)
C3	0.052(3)	0.057(3)	0.051(3)	0.011(2)	-0.011(2)	-0.009(2)
C4	0.061(3)	0.053(3)	0.030(2)	0.011(2)	-0.007(2)	-0.002(2)
C5	0.028(2)	0.041(2)	0.039(2)	0.009(2)	-0.002(2)	-0.002(2)
C6	0.037(3)	0.041(2)	0.043(3)	0.007(2)	0.006(2)	0.009(2)
C7	0.031(2)	0.039(2)	0.042(3)	0.0055(19)	0.004(2)	0.012(2)
C8	0.037(3)	0.057(3)	0.059(3)	0.011(2)	0.008(3)	0.018(2)
C9	0.041(3)	0.072(4)	0.072(4)	0.005(2)	-0.013(3)	0.043(3)
C10	0.048(4)	0.067(4)	0.059(4)	-0.019(2)	-0.017(3)	0.031(3)
C11	0.038(3)	0.048(3)	0.051(3)	-0.016(2)	-0.003(2)	0.014(2)
C12	0.054(3)	0.032(2)	0.039(2)	-0.012(2)	0.006(2)	0.011(2)
C13	0.049(3)	0.032(2)	0.031(2)	-0.009(2)	0.007(2)	-0.003(2)
C14	0.042(3)	0.035(2)	0.036(2)	-0.005(2)	0.004(2)	-0.001(2)
C15	0.057(3)	0.037(2)	0.022(2)	-0.017(2)	0.002(2)	0.000(2)
C16	0.055(3)	0.051(3)	0.062(3)	0.025(2)	0.011(3)	0.001(3)
C17	0.135(6)	0.052(3)	0.036(3)	-0.045(3)	0.007(3)	-0.010(2)
C18	0.125(5)	0.071(4)	0.032(2)	-0.038(3)	0.013(3)	-0.012(2)
C19	0.081(4)	0.050(3)	0.055(3)	-0.029(3)	0.025(3)	-0.011(2)
C20	0.047(3)	0.040(2)	0.050(3)	-0.014(2)	0.005(2)	-0.010(2)
C21	0.147(7)	0.070(4)	0.037(3)	0.059(4)	0.029(3)	0.001(3)
C22	0.307(16)	0.064(5)	0.045(4)	0.052(7)	0.057(7)	0.013(4)
C23	0.055(4)	0.080(4)	0.052(3)	0.028(3)	0.015(2)	0.032(3)
C24	0.046(3)	0.087(4)	0.055(3)	0.017(3)	0.013(3)	0.036(3)

The general temperature factor expression :

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

other across the anthracene ring. The conformation of **1** was similar to that of *N9,N9,N10,N10*-tetraethyl-9,10-anthracenedimethanamine.¹³⁾ The dihedral angles between the least-squares anthracene plane A (defined by C1/C2/C3/C4/C5/C6/C7/C8/C9/C10/C11/C12/C13/C14) and the morpholine ring (defined by N1/C17/C18/O1/C19/C20) and between plane A and the morpholine ring (defined by N2/C21/C22/O2/C23/C24) are 86.6(1) $^\circ$ and 73.8(2) $^\circ$, respectively, which are close to that (97.46(4) $^\circ$)¹⁶⁾ of

9-(thiomorpholinomethyl)anthracene. The morpholine parts of **1** have a chair conformation (C17—N1—C20—C19 58.7(5)°, C20—N1—C17—C18—65.9(6)°, C18—O1—C19—C20 62.1(6)°, C19—O1—C18—C17—65.0(5)°, N1—C17—C18—O1 68.7(6)°, O1—C19—C20—N1—60.7(6)°, C22—O2—C23—C24—51.8(8)°, C23—O2—C22—C21 47.3(11)°, C21—N2—C24—C23—57.9(6)°, C24—N2—C21—C22 46.4(8)°, N2—C21—C22—O2—43.9(11)°, O2—C23—C24—N2 57.4(7)°). The anthracene ring system of **1** is close to the N atom of the morpholine group ; the distance between C13 and N1 [2.501(6) Å] is shorter than the sum of their van der Waals radii (3.25 Å),²⁹ indicating that PET from the N atom in the morpholine group to excited anthracene system can occur efficiently. The selected geometric parameters were shown in Table 3.

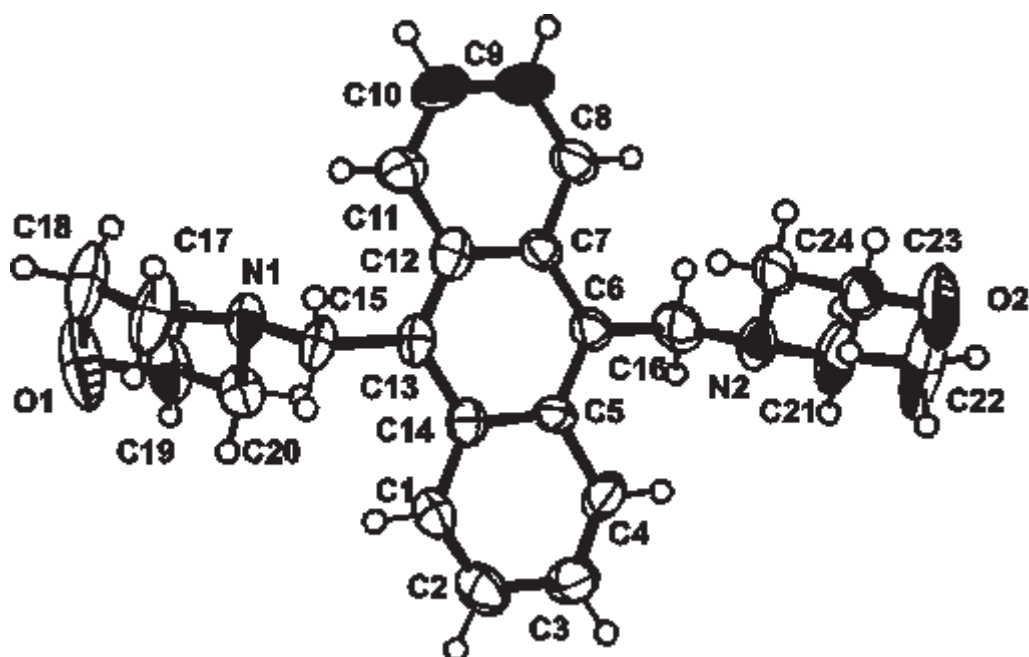


Fig. 2. An ORTEP drawing of **1** showing 50% probability displacement ellipsoids.

Table 3. Selected geometric parameters (Å, °)

O1—C18	1.552(8)	O1—C19	1.416(8)
O2—C22	1.240(12)	O2—C(23)	1.425(8)
N1—C15	1.474(6)	N1—C17	1.462(7)
N1—C20	1.449(7)	N2—C16	1.472(7)
N2—C21	1.475(7)	N2—C(24)	1.466(8)
C1—C2	1.335(8)	C1—C14	1.426(7)
C2—C3	1.449(9)	C3—C4	1.338(8)

C4—C5	1.430(7)	C5—C6	1.418(7)
C5—C14	1.437(7)	C6—C7	1.400(7)
C6—C16	1.493(8)	C7—C8	1.448(7)
C7—C12	1.448(7)	C8—C9	1.381(9)
C9—C10	1.370(9)	C10—C11	1.369(8)
C11—C12	1.429(7)	C12—C13	1.406(7)
C13—C14	1.409(7)	C13—C15	1.545(6)
C17—C18	1.512(9)	C19—C20	1.502(8)
C21—C22	1.572(11)	C23—C24	1.511(9)
C18—O1—C19	104.4(4)	C22—O2—C23	115.1(6)
C15—N1—C17	109.8(4)	C15—N1—C20	109.4(4)
C17—N1—C20	107.6(4)	C16—N2—C21	109.3(4)
C16—N2—C24	114.0(4)	C21—N2—C24	111.1(5)
C2—C1—C14	122.1(5)	C1—C2—C3	121.1(5)
C2—C3—C4	117.6(5)	C3—C4—C5	124.0(5)
C4—C5—C6	121.2(4)	C4—C5—C14	117.3(4)
C6—C5—C14	121.5(4)	C5—C6—C7	118.6(4)
C5—C6—C16	118.4(5)	C7—C6—C16	123.0(5)
C6—C7—C8	121.8(4)	C6—C7—C12	120.9(4)
C8—C7—C12	117.3(4)	C7—C8—C9	121.1(5)
C8—C9—C10	119.7(6)	C9—C10—C11	123.3(6)
C10—C11—C12	119.6(5)	C7—C12—C11	118.9(4)
C7—C12—C13	119.4(4)	C11—C12—C13	121.7(4)
C12—C13—C14	120.8(4)	C12—C13—C15	118.0(4)
C14—C13—C15	121.2(4)	C1—C14—C5	117.8(4)
C1—C14—C13	123.4(4)	C5—C14—C13	118.8(4)
N1—C15—C13	111.8(3)	N2—C16—C6	112.4(4)
N1—C17—C18	107.8(5)	O1—C18—C17	105.0(5)
O1—C19—C20	113.0(4)	N1—C20—C19	109.3(4)
N2—C21—C22	107.2(5)	O2—C22—C21	121.7(7)
O2—C23—C24	109.9(5)	N2—C24—C23	110.7(4)
C18—O1—C19—C20	62.1(6)	C19—O1—C18—C17	-65.0(5)
C22—O2—C23—C24	-51.8(8)	C23—O2—C22—C21	47.3(11)
C15—N1—C17—C18	175.1(5)	C17—N1—C15—C13	-174.0(5)
C15—N1—C20—C19	177.9(4)	C20—N1—C15—C13	68.2(5)
C17—N1—C20—C19	58.7(5)	C20—N1—C17—C18	-65.9(6)
C16—N2—C21—C22	173.1(6)	C21—N2—C16—C6	169.9(5)

C16—N2—C24—C23	178.0(5)	C24—N2—C16—C6	-65.0(6)
C21—N2—C24—C23	-57.9(6)	C24—N2—C21—C22	46.4(8)
C2—C1—C14—C5	-2.3(7)	C2—C1—C14—C13	177.6(5)
C14—C1—C2—C3	3.8(8)	C1—C2—C3—C4	-2.1(8)
C2—C3—C4—C5	-1.0(8)	C3—C4—C5—C6	-177.3(5)
C3—C4—C5—C14	2.4(8)	C4—C5—C6—C7	-179.2(4)
C4—C5—C6—C16	1.5(7)	C4—C5—C14—C1	-0.8(7)
C4—C5—C14—C13	179.3(4)	C6—C5—C14—C1	179.0(4)
C6—C5—C14—C13	-0.9(7)	C14—C5—C6—C7	1.0(7)
C14—C5—C6—C16	-178.3(4)	C5—C6—C7—C8	177.9(4)
C5—C6—C7—C12	-0.6(7)	C5—C6—C16—N2	-74.8(6)
C7—C6—C16—N2	105.9(6)	C16—C6—C7—C8	-2.9(8)
C16—C6—C7—C12	178.7(4)	C6—C7—C8—C9	-179.6(5)
C6—C7—C12—C11	-180.0(4)	C6—C7—C12—C13	0.1(6)
C8—C7—C12—C11	1.5(7)	C8—C7—C12—C13	-178.4(4)
C12—C7—C8—C9	-1.1(7)	C7—C8—C9—C10	0.4(8)
C8—C9—C10—C11	-0.2(7)	C9—C10—C11—C12	0.7(9)
C10—C11—C12—C7	-1.3(7)	C10—C11—C12—C13	178.6(5)
C7—C12—C13—C14	0.0(6)	C7—C12—C13—C15	179.1(4)
C11—C12—C13—C14	-179.9(3)	C11—C12—C13—C15	-0.9(7)
C12—C13—C14—C1	-179.5(4)	C12—C13—C14—C5	0.4(7)
C12—C13—C15—N1	70.5(6)	C14—C13—C15—N1	-110.4(5)
C15—C13—C14—C1	1.5(7)	C15—C13—C14—C5	-178.6(4)
N1—C17—C18—O1	68.7(6)	O1—C19—C20—N1	-60.7(6)
N2—C21—C22—O2	-43.9(11)	O2—C23—C24—N2	57.4(7)

An intermolecular C-H $\cdots\pi$ interaction is observed in **1** as shown in **Fig. 3** and **Table 4**. The distance between atom H4 and the centroid C_g (defined by C5ⁱ/C6ⁱ/C7ⁱ/C12ⁱ/C13ⁱ/C14ⁱ) (symmetry code : (i) 1/2+x, -y, z) is 3.213 Å, which is longer than the intermolecular C-H $\cdots\pi$ interaction observed in 2-methacryloxytropone [H \cdots C : 2.84 Å].³⁰⁾

There is an intermolecular C-H \cdots O interaction in **1**. The distances between atom C21-H22 and O1ⁱⁱ is 2.514 Å (symmetry code : (ii) 3/2-x, y, z-1/2), which is shorter than those of 2-methacryloxytropone [2.49-2.71 Å]²⁸⁾ and ethyl 9-methoxy-2-oxo-2 H-1-benzopyran-3-carboxylate [2.57-2.72 Å].³¹⁾

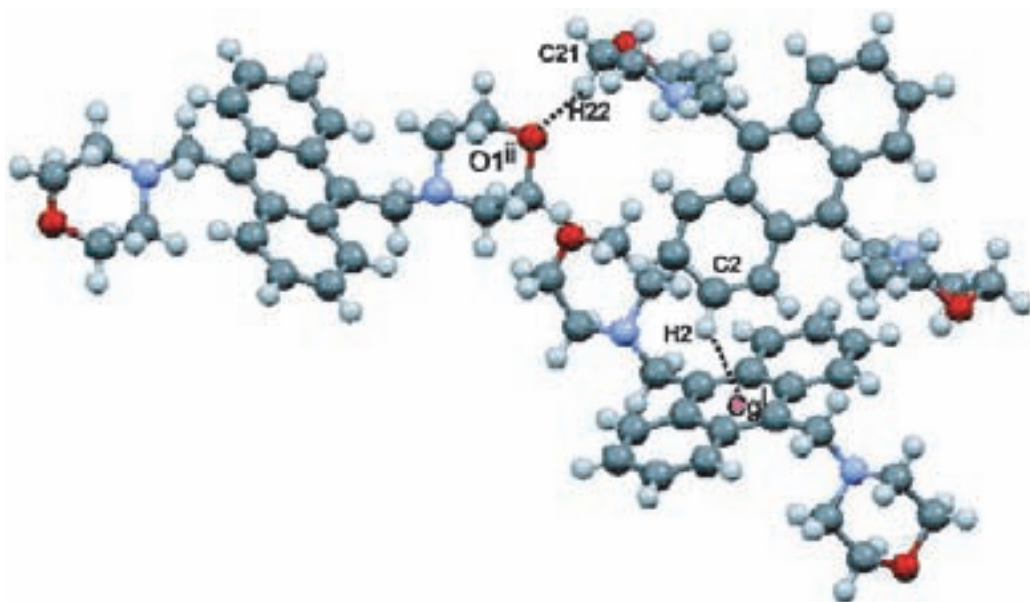


Fig. 3. Intermolecular C-H \cdots π and C-H \cdots O interactions of **1**.

Table 4. C-H \cdots π and C-H \cdots O bond geometry (\AA , $^\circ$)

D	H	A	D-H	H \cdots A	D \cdots A	D-H \cdots A	Symmetry codes
C2	H2	Cg1 ⁱ	0.950	3.213	3.717	115	(i) 1/2+x, -y, z
C21	H22	O1 ⁱⁱ	0.990	2.514	3.381	146	(ii) 3/2-x, y, z-1/2

In conclusion, the crystal structure of 4-(9-anthracenylmethyl)thiomorpholine (**1**) was elucidated by X-ray crystallographic analysis. Intermolecular C-H \cdots π and C-H \cdots O interactions help stabilized the crystal packing.

4. References and Notes

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