J. Am. Chem. Soc. 1992, 114, 8414-8416

A New Three-Dimensional Cycloaddition Compound and Its Inclusion Complexes Formed by 1,3-Dipolar Cycloaddition Reaction of *p*-Phenylenebis(3-sydnone) and *N*-Phenylmaleimide

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Abstract: A new three-dimensional heterocyclic compound was synthesized from *p*-phenylenebis(3-sydnone) and *N*-phenylmaleimide. This compound incorporates solvent molecules into the crystal lattice to form new inclusion complexes. The structure and the desolvation process were examined by the use of X-ray diffraction, thermogravimetry, differential thermal analysis, FT-IR spectra, ^1H NMR spectra, and solid-state high-resolution ^{13}C NMR spectra. The host compound may possibly be one of the precursory materials of novel ladder polymers.

Sydnones are very reactive agents and have been widely used for the syntheses of a number of cycloaddition compounds.[1-7] We found previously that 3-phenylsydnone reacts with *N*-phenylmaleimide to produce a diimide derivative of tetracarboxylic acid, 3,5,9,11-tetraoxo-4,10,13-triphenyl-1,4,10,13-tetrazatetracyclo[5.5.1.0.^{2,6}0^{8,12}]tridecane.[8,9] We now apply this method of synthesis to a more complex 1:4 cycloaddition reaction between *p*-phenylenebis(3-sydnone) and *N*-phenylmaleimide (Scheme I).

A mixture of *p*-phenylenebis(3-sydnone), which was synthesized from *p*-phenylenediamine by a standard method[10] and *N*-phenylmaleimide[11] with a molar ratio of 1:4, was dissolved in Me_2SO, DMA, or DMF[12] and stirred for 60 min at 130 °C; white polycrystalline crystals deposited were filtered and recrystallized from the appropriate solvent.

The product was a new compound, 3,5,9,11-tetraoxo-4,10-diphenyl-(1,4-bis(1,4,10,13-tetrazatetracyclo[5.5.1.0.^{2,6}0^{8,12}]-13-tridecyl)benzene) (I). However, chemical analysis,[13] thermogravimetry (TG), and differential thermal analysis (DTA) of the neat crystalline product indicated that it is a new type of inclusion complex between the host compound I and each solvent with the composition of 1:2.

The TG and DTA experiments were carried out using Seiko Model SSC-560H thermal analyses instruments under a nitrogen atmosphere from room temperature to about 350 °C. Table I records the results of DTA and TG of three complexes. In each complex, the weight of the specimen began to decrease at about 180 °C, and a remarkable endothermic peak was detected at the temperature cited in Table I. The overall weight loss at this stage corresponds to complete desolvation. The remaining host compound I is a pale yellow powder and stable up to 324 °C, at which temperature it decomposes with emission of an appreciable amount of heat. Pure I can also be obtained on heating at 200 °C under reduced pressure for 2 h. The inclusion complex can be reproduced by dissolving I in the appropriate solvent.

The crystal structures of the I-DMA and I-DMF complexes were determined by a single-crystal X-ray diffraction method.

Crystal data. I-DMA: $C_{48}H_{34}N_8O_8{\cdot}2C_4H_9NO$, mol wt = 1025.09, monoclinic, $P2_1/c$, $a = 13.720$ (5) Å, $b = 12.347$ (5) Å, $c = 17.257$ (9) Å, $\beta = 118.74$ (4)°, $V = 2563$ (2) Å^3, $Z = 2$, d(calcd) = 1.328 g cm^{-3}, $R = 0.070$ for 1867 reflections. I-DMF: $C_{48}H_{34}N_8O_8{\cdot}2C_3H_7NO{\cdot}{}^1/_2(H_2O)$, mol wt = 1006.05, monoclinic, $P2_1/c$, $a = 13.692$ (5) Å, $b = 12.231$ (7) Å, $c = 17.140$ (2) Å, $\beta = 118.82$ (2)°, $V = 2515$ (2) Å^3, $Z = 2$, d(calcd) = 1.328 g cm^{-3}, $R = 0.061$ for 2363 reflections. Intensity data were collected on a Rigaku AFC-5R diffractometer using graphite-mono-

Scheme I

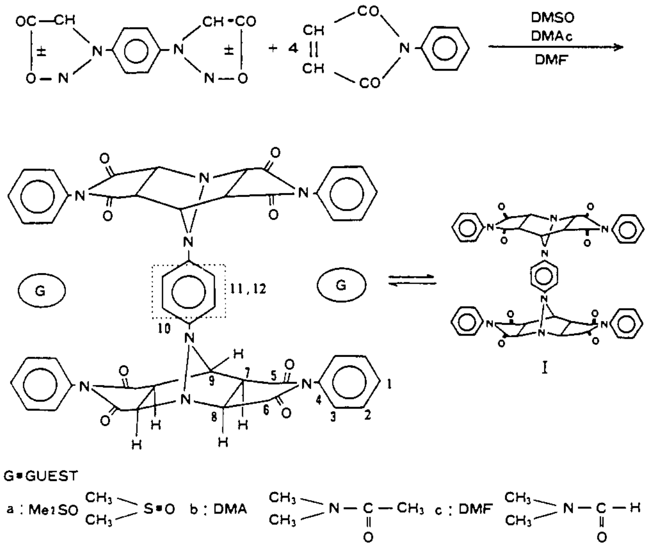

Table I. Desolvation Temperatures and Weight Losses of Three Inclusion Complexes Measured by the DTA-TG Method

guest	temp/°C	wt loss/%[a]
Me_2SO	243	16 (15.5)
DMA	193	16 (17.0)
DMF	189	13 (14.6)

[a] Calculated weight loss in the release stage of two guest molecules.

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(12) Me_2SO: dimethylsulfoxide; DMA: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide.

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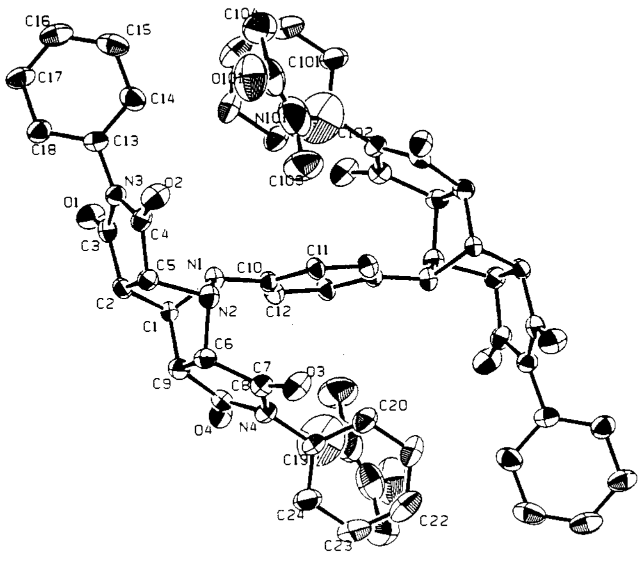

Figure 1. ORTEP plot of I–DMA with the atom numbering system. Ellipsoids are scaled to enclose 30% of the electronic density.

chromatized Cu Kα radiation (λ = 1.541 78 Å). The structures were solved by the use of the program MULTAN-84.[14] The guest molecule was assumed to be disordered because the different sites of the disordered molecules were not located in a difference Fourier map. The structure was refined by the block-diagonal least-squares method using the positional and anisotropic thermal parameters for the non-H atoms. Hydrogen atoms, excluding those of the guest molecule, were refined with the fixed temperature factors set equal to B_{eq}'s of the bonded atoms. Absorption corrections were applied after isotropic least-squares refinement by an empirical method based on the differences between the observed and calculated structure factors.[14] Atomic scattering factors were evaluated by $f = \Sigma[a_i \exp(-b_i\lambda^{-2} \sin^2\theta)] + c$ (i = 1, ... 4).[15] Weights were taken as $w = [\sigma^2(F_o) + 0.0042|F_o|^2] - 1$ for the reflections with $w^{1/2}|\Delta F| < 4$, and $w = 0$ otherwise. No peaks larger than 0.2 e Å^{-3} were found in the last difference electron density map. The comparatively large R values may be due to the poor quality of intensity data measured by using very small and inferior crystals and to the disordered structure of the guest molecules. Computations using the programs PLUTO[16] and KPACK86 SHIONOGI[17] were performed on a FACOM X-730 computer at Shionogi Research Laboratories.

A perspective view of the host and the guest molecules in I–DMA (with a different numbering system from that of Scheme I) is shown in Figure 1, and some of the bond distances and bond angles are listed in Table II. The host molecule occupies a centrosymmetric site with mostly normal bond lengths and angles. The two phenyl rings, C(13)–C(18) and C(19)–C(24), are twisted around the N(3)–C(13) and N(4)–C(19) bonds by 58.4 (3)° and 68.1 (3)°, respectively.

The crystal structure viewed down the a-axis is presented in Figure 2, in which the two guest molecules are enclathrated in a cavity formed by the 5- and 6-membered rings of the surrounding four host molecules. Some anomalous bond lengths and large temperature factors in the DMA guest molecule suggest that this molecule is in a dynamic disordered state. The structure of the I–DMF complex is similar to that of I–DMA, but the guest molecule in I–DMF is disordered at the two related locations, approximately by a 2-fold axis imagined to lie along the N–O direction. The disordering model was confirmed on a differential Fourier map for I–DMF but not for I–DMA.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) in I–DMA and I–DMF

	I–DMA	I–DMF
	Bond Lengths	
O(1)–C(3)	1.202 (8)	1.216 (7)
O(2)–C(4)	1.215 (8)	1.213 (6)
N(1)–N(2)	1.482 (8)	1.463 (5)
N(1)–C(1)	1.469 (8)	1.453 (5)
N(1)–C(10)	1.422 (8)	1.432 (5)
N(2)–C(5)	1.537 (8)	1.508 (6)
N(3)–C(3)	1.401 (8)	1.389 (6)
N(3)–C(4)	1.370 (8)	1.376 (5)
N(3)–C(13)	1.441 (9)	1.437 (6)
C(1)–C(2)	1.501 (8)	1.518 (6)
C(2)–C(3)	1.514 (8)	1.507 (7)
C(2)–C(5)	1.542 (8)	1.550 (6)
C(4)–C(5)	1.507 (8)	1.515 (6)
O(101)–C(101)	1.412 (17)	1.22 (1)
N(101)–C(101)	1.150 (19)	1.38 (1)
N(101)–C(102)	1.578 (19)	1.47 (2)
N(101)–C(103)	1.546 (16)	1.39 (2)
C(101)–C(104)	1.495 (19)	
	Bond Angles	
N(2)–N(1)–C(1)	98.3 (4)	98.5 (3)
N(2)–N(1)–C(10)	117.6 (5)	117.7 (3)
C(1)–N(1)–C(10)	118.7 (5)	118.9 (3)
N(1)–N(2)–C(5)	98.1 (4)	98.8 (3)
C(5)–N(2)–C(6)	103.0 (4)	104.1 (3)
C(3)–N(3)–C(4)	112.4 (5)	112.9 (4)
C(3)–N(3)–C(13)	123.0 (5)	122.5 (4)
N(1)–C(1)–C(2)	97.9 (4)	98.4 (3)
C(2)–C(1)–C(9)	107.0 (5)	106.4 (3)
C(1)–C(2)–C(3)	112.0 (5)	112.2 (4)
C(1)–C(2)–C(5)	103.7 (4)	102.0 (3)
C(3)–C(2)–C(5)	103.2 (4)	104.0 (3)
O(1)–C(3)–N(3)	123.6 (6)	124.4 (5)
O(1)–C(3)–C(2)	127.2 (6)	126.4 (5)
N(3)–C(3)–C(2)	109.1 (5)	109.2 (4)
O(2)–C(4)–N(3)	124.4 (6)	124.7 (4)
O(2)–C(4)–C(5)	126.8 (6)	126.6 (4)
N(3)–C(4)–C(5)	108.7 (5)	108.7 (3)
N(2)–C(5)–C(2)	102.5 (4)	103.1 (3)
N(2)–C(5)–C(4)	112.7 (5)	112.9 (3)
C(2)–C(5)–C(4)	105.9 (5)	104.9 (3)

The structures of present complexes show clearly that the host molecule is bulky enough to provide a large void for the enclathration of small molecules; a number of similar structures have been so far reported.[18-20] It seems that the skeletal structure is very stable, and so it can enclathrate various guests without any specific interaction such as hydrogen bonding.[18] Therefore, the clathrates may be used for the separation of chemically inert materials.[20,21] The alignment of the guest molecules in the void is probably governed by the dipolar interaction between the guest molecules as well as the steric effect of the cavity.

Fourier transform infrared spectra using the KBr disk method obtained on a Perkin-Elmer Model 1750 spectrometer confirmed also the existence of nearly free solvent molecules in the inclusion complexes. For example, the I–Me_2SO complex gave a strong and relatively sharp band at 1046 cm^{-1} due to S–O stretching in Me_2SO guest and another band at 700 cm^{-1} characteristic of Me_2SO, but pure I did not give these bands. The main bands due to the host molecule were observed at 1780 and 1710 cm^{-1} (imide C=O), 1380 cm^{-1} (imide C–N), and 1205 cm^{-1} ($C_{aliphatic}$–N).

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(13) Results of chemical analyses: (a) I–Me_2SO. Found: C, 62.10; H, 4.50; N, 11.13; S, 6.54; Calcd for $C_{48}H_{34}N_8O_8 + 2C_2H_6OS$: C, 62.02; H, 4.60; N, 11.13; S, 6.37. (b) I–DMA. Found: C, 65.64; H, 5.03; N, 13.70; Calcd for $C_{48}H_{34}N_8O_8 + 2C_4H_9NO$: C, 65.61; H, 5.11; N, 13.66. (c) I–DMF. Found: C, 65.17; H, 4.65; N, 14.30; Calcd for $C_{48}H_{34}N_8O_8 + 2C_3H_7NO$: C, 65.05; H, 4.85; N, 14.05.

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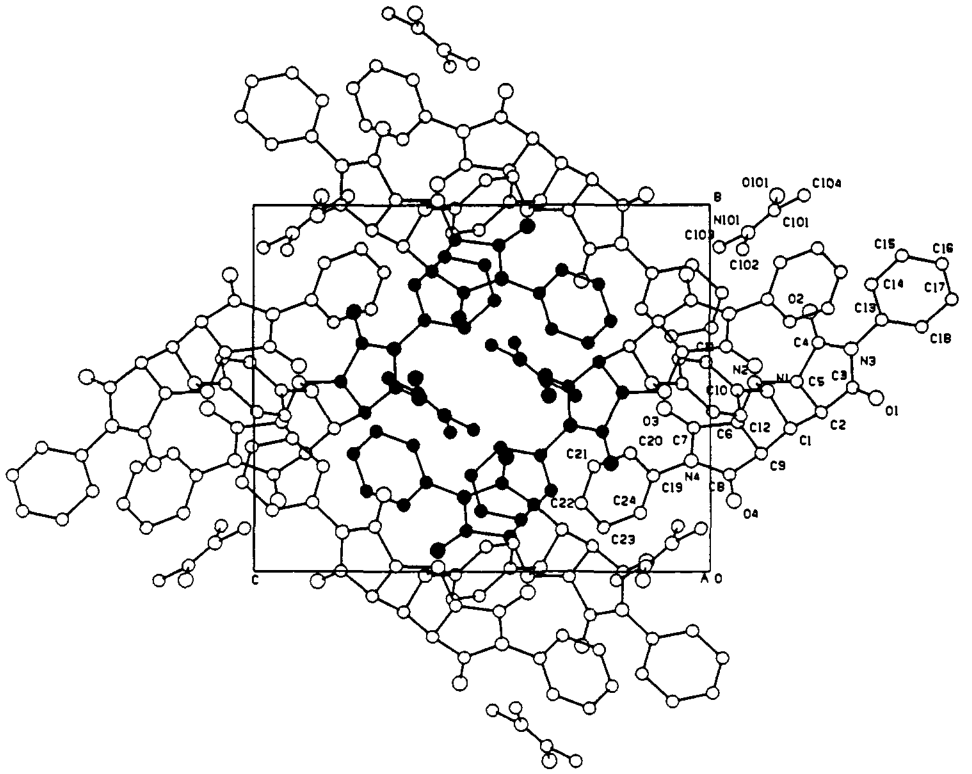

Figure 2. Crystal structure of I–DMA viewed down the *a*-axis.

Table III. ^{13}C NMR Chemical Shifts[a] in I and the Inclusion Complexes

I[b]	I[c]	I–Me_2SO	I–DMA	I–DMF[d]	assignment
			21.8	30.2	CH_3, guest
		38.8	36.7	35.4	CH_3, guest
				48.0	8
50.6	50.3	49.6	49.7	49.7	
64.7	66.8	62.8	61.4	62.8	9
69.0	68.6	69.2	66.8	68.9	7
		115.3	115.8	115.0	11,12
117.6	117.7	118.1	119.3	118.6	
127.4	125.6	127.2			1,2,3,4
	129.0	129.0	129.4	129.5	
130.6		130.6		131.9	
	132.4	132.2			
139.0	139.0	137.9	138.6	139.0	10
				162.6	C=O, guest
171.6	171.1	171.5		172.6	5,6
	172.7	173.2	173.4[e]	176.2	

[a] Chemical shift in ppm from TMS with uncertainty of ±0.2 ppm at 21 °C. [b] Pure host I obtained by desolvation of I–Me_2SO. [c] Pure host I obtained by desolvation of I–DMF. [d] Specimen contains a trace of water. [e] C=O's in host and guest molecules. All ^{13}C NMR spectra were measured at 50.3 MHz on a Bruker MSL-200 spectrometer using CP/MAS (cross polarization–magic angle spinning) and total sideband suppression techniques.

Other unassigned bands were observed at 1500 cm^{-1} and between 490 and 920 cm^{-1} (8–10 bands). The C–H stretching gave a broad band at 3300 cm^{-1}.

In order to study the guest–host interaction and the role of the guest molecules in the crystal lattice stabilization, we conducted the proton NMR experiment for a solution of I in DMF-d_7 at 270 MHz and the high-resolution ^{13}C NMR for I and the inclusion complexes in the solid state at 50.3 MHz. The ^1H spectra obtained were relatively simple and can be accounted for by the structure in Figure 1. The ^1H chemical shifts in ppm from TMS are 3.72 (assigned to H_7 and $H_{7'}$), 4.67 (H_8, $H_{8'}$), 5.69 (H_9), 6.83–7.28 (aromatic protons). The relative intensity ratio was 2:2:1:12. The H_8 and H_9 give signals at relatively low fields due probably to the deshielding effect by the nearby nitrogen or oxygen. It seems that no specific interaction such as site-specific hydrogen bonding between I and the solvent molecules occurs in the solution.

The results of the ^{13}C NMR obtained using a Bruker MSL-200 spectrometer are listed in Table III. All spectra were assigned on the basis of the structure in Figure 1 with the help of the dipolar dephasing technique for the ^{13}C spectra. It is noted that the chemical shift of the central aromatic carbons (C_{11} and C_{12}) splits into two on forming the inclusion complexes. It is also interesting to see that the spectrum of pure I depends on the preparation; the spectrum of I made from I–Me_2SO is simpler than the one from I–DMF. This fact suggests that the desolvation brings about some distortion of the molecular structure but the degree of the distortion may depend on the guest molecule. The dipolar dephasing experiments for the three complexes show that the dipolar interaction between ^1H and ^{13}C is not effective in the guest molecules. This suggests that rotational motion of the guest molecules is highly excited at room temperature, consistent with the results of the X-ray analysis.

It is important to see that I keeps its structure at up to 324 °C even after the desolvation occurs. We have just found that I is closely related to a reactive derivative which undergoes a polymerization reaction at high temperatures and produces a new type of ladder polymers. Work on this subject as well as further investigation of the host-guest interactions in the complex compounds of I is in progress.

Registry No. I, 132630-31-0; I-DMA, 132697-52-0; I-DMF, 132697-53-1; I-Me_2SO, 132630-32-1; *p*-phenylenebis(3-sydnone), 10301-11-8; *N*-phenylmaleimide, 941-69-5.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic temperature factors, and bond distances and angles for I–DMA and I–DMF (12 pages); listing of observed and calculated structure factors of the I–DMA and I–DMF (18 pages). Ordering information is given on any current masthead page.