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Structure of *N,N'*-Dityrityl-2,5-diketopiperazine and its 1:1 Inclusion Complex with Methylene Chloride

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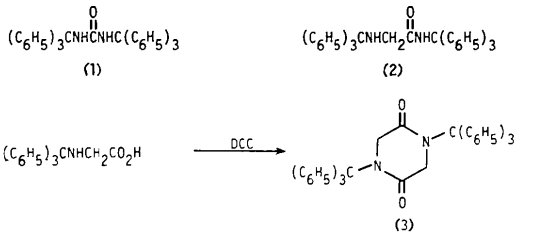
Abstract. *N,N'*-Dityrityl-2,5-diketopiperazine: $C_{42}H_{34}N_2O_2$, $M_r = 598{\cdot}7$, monoclinic, $P2_1/c$, $a = 11{\cdot}737\ (2)$, $b = 16{\cdot}199\ (6)$, $c = 17{\cdot}710\ (3)$ Å, $\beta = 108{\cdot}37\ (1)°$, $V = 3196{\cdot}6\ (15)$ Å^3, $Z = 4$, $D_x = 1{\cdot}245$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}7$ cm^{-1}, $F(000) = 1264$, room temperature. Its methylene chloride complex: $C_{42}H_{34}N_2O_2.CH_2Cl_2$, $M_r = 683{\cdot}7$, triclinic, $P\bar{1}$, $a = 12{\cdot}193\ (5)$, $b = 12{\cdot}378\ (9)$, $c = 12{\cdot}670\ (5)$ Å, $\alpha = 106{\cdot}74\ (4)$, $\beta = 104{\cdot}01\ (3)$, $\gamma = 90{\cdot}38\ (5)°$, $V = 1770{\cdot}7\ (17)$ Å^3, $Z = 2$, $D_x = 1{\cdot}282$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2{\cdot}2$ cm^{-1}, $F(000) = 716$, room temperature. R values respectively 0·047 and 0·109 for 2578 and 1940 observed reflections. The *N,N'*-dityrityldiketopiperazine molecule has a strained and nearly rigid conformation and its molecular surface is not ellipsoidal, but has thick ends and a thin center. Two different types of intermolecular packing were observed. In crystals of the free compound the molecules interpenetrate each other, with the trityl groups of one species lying above the central ring of an adjacent molecule. In the inclusion complex the host molecules are arranged in layers parallel to the *ab* plane of the unit cell, with the trityl groups in contact, and the space between the diketopiperazine rings filled by CH_2Cl_2.

Introduction. We have used trityl (triphenylmethyl) groups as large rigid 'spacers' in the design of hosts for crystalline host–guest complexes (Hart, Lin & Ward, 1984, 1985; Goldberg, Lin & Hart, 1984, 1985). *N,N'*-Dityrylurea (1) is an excellent host for such complexes. As a slight variant on this structure, we sought to insert a methylene group in the chain by preparing *N,N'*-dityrylglycinamide (2). Treatment of a mixture of *N*-tritylglycine and tritylamine with dicyclohexylcarbodiimide (DCC) did not, however, give the desired (2). Instead the product was *N,N'*-dityryldiketopiperazine (3), which was also formed in good yield when the tritylamine was omitted. Somewhat to our surprise since it did not conform to our original host design (Hart *et al.*, 1984) (3) did form complexes with certain small molecules such as methylene chloride. We report here on the single-crystal X-ray structure of (3) without a guest, and of its 1:1 complex with methylene chloride (4). [In later experiments, we did succeed in preparing (2), and related amino-acid derivatives by another method; their behavior as hosts will be reported later.]



Experimental. A solution containing 1·4 g (4·4 mmol) of *N*-tritylglycine (Zervas & Theodoropoulos, 1956) and 0·91 g (4·4 mmol) of DCC in 50 ml of anhydrous methylene chloride was stirred at room temperature overnight. The solvent was removed under vacuum to leave a white solid which was chromatographed on silica gel with 40% ethyl acetate in hexane as eluent, to give 1·0 g (76%) of *N,N'*-dityryl-2,5-diketopiperazine (3), m.p. 543 K (dec.). For (3): ^{1}H NMR (250 MHz, $CDCl_3$) δ 3·85 (*s*, 4 H), 7·2–7·5 (*m*, 30 H); ^{13}C NMR (62·9 MHz, $CDCl_3$) δ 52·43, 76·33, 126·93, 128·04, 128·75, 142·23, 167·99; IR (KBr) 3050 (*m*), 2930 (*m*), 2860 (*m*), 1680 (*s*), 1620 (*m*), 1490 cm^{-1} (*w*); mass spectrum, *m/e* (relative intensity) 598 (5), 355 (5), 243 (100). Recrystallization of (3) from methylene chloride gave the 1:1 complex (4), with the same m.p. (dec.).

Crystallographic analysis: crystals used ~0·3 × 0·4 × 0·4 mm (3) and ~0·2 × 0·2 × 0·3 mm (4); cell constants determined by least-squares procedures applied to 25 reflections with $10 < \theta < 16°$ for (3) and to 22 reflections with $9 < \theta < 11°$ for (4). Diffraction data measured at *ca* 291 K, Enraf–Nonius CAD-4 diffractometer, graphite monochromator, Mo $K\alpha$ radiation, ω–2θ scans, scan rate 1–5° min^{-1}, scan range 1·2 + 0·3tanθ°. For (3) 6441 reflections collected to θ_{max}

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$= 25°$, range of hkl: $0 \le h \le 13$, $0 \le k \le 19$, $-21 \le l \le 21$, 4336 unique with $I > 0$ ($R_{int} = 0.047$). For (4) 5184 reflections measured to $\theta = 23°$, range of hkl: $0 \le h \le 13$, $-13 \le k \le 13$, $-13 \le l \le 13$, 3724 unique with a positive intensity ($R_{int} = 0.035$). The crystals were checked for deterioration, monitoring the intensities of three standard reflections from different zones of the reciprocal space. In (3) deterioration was found to be negligible during the measurements. In (4) an appropriate correction of the data was required to account for the linear (in time) and nearly equal significant decrease in the intensities of the standards during the experiment. Data not corrected for absorption or secondary extinction effects. Final refinement calculations based on 2578 (3) and 1940 (4) reflections with $F_o^2 \ge 3\sigma(F_o^2)$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

The two structures were solved by a combination of direct and Fourier methods. Subsequent least-squares refinement of (3) included the positional and anisotropic thermal parameters of all the non-H atoms. Two types of constraints were applied to the refinement of (4). The relatively poor quality of the data and the substantial number of weak reflections (which were excluded from the calculations) led us to decrease the number of refined parameters by treating the six phenyl rings as geometrically constrained rigid groups. Moreover, the C and Cl atoms of methylene chloride were refined isotropically in view of the apparent dynamic disorder (broad thermal motion) exhibited by the guest species. (Considering the significant deterioration of the crystal during the measurements, the large parameters of thermal motion obtained for the methylene chloride can also be indicative of only a fractional occupancy of the guest sites in the crystal lattice.) All remaining non-H atoms in (4) were allowed anisotropic motions. In both structures all H atoms were located in calculated positions, and assigned a fixed isotropic temperature

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for* (3)

U_{eq} is one third of the trace of the orthogonalized U_{ij} matrix.

	x	y	z	U_{eq}(Å²)
N(1)	0·3311 (2)	0·3158 (2)	0·2114 (2)	0·0355
C(2)	0·3279 (3)	0·3233 (2)	0·2874 (2)	0·0396
O(3)	0·2405 (2)	0·3454 (2)	0·3068 (1)	0·0538
C(4)	0·4451 (3)	0·3098 (2)	0·3514 (2)	0·0410
N(5)	0·5499 (2)	0·3191 (2)	0·3238 (1)	0·0334
C(6)	0·5450 (3)	0·2717 (2)	0·2590 (2)	0·0352
O(7)	0·6303 (2)	0·2447 (2)	0·2416 (1)	0·0512
C(8)	0·4200 (3)	0·2559 (2)	0·2039 (2)	0·0429
C(9)	0·2204 (3)	0·3305 (2)	0·1420 (2)	0·0361
C(10)	0·1672 (3)	0·4158 (2)	0·1497 (2)	0·0352
C(11)	0·2333 (3)	0·4781 (2)	0·1976 (2)	0·0447
C(12)	0·1840 (3)	0·5556 (2)	0·2006 (2)	0·0509
C(13)	0·0669 (4)	0·5723 (2)	0·1536 (2)	0·0510
C(14)	0·0023 (3)	0·5116 (2)	0·1041 (2)	0·0463
C(15)	0·0518 (3)	0·4344 (2)	0·1019 (2)	0·0410
C(16)	0·1355 (3)	0·2576 (2)	0·1398 (2)	0·0378
C(17)	0·0413 (3)	0·2639 (2)	0·1716 (2)	0·0479
C(18)	−0·0269 (3)	0·1957 (2)	0·1761 (2)	0·0577
C(19)	−0·0014 (4)	0·1194 (3)	0·1501 (3)	0·0646
C(20)	0·0910 (4)	0·1117 (2)	0·1190 (2)	0·0603
C(21)	0·1598 (3)	0·1802 (2)	0·1139 (2)	0·0470
C(22)	0·2563 (3)	0·3392 (2)	0·0658 (2)	0·0403
C(23)	0·1849 (3)	0·3087 (2)	−0·0065 (2)	0·0482
C(24)	0·2148 (4)	0·3230 (3)	−0·0759 (2)	0·0634
C(25)	0·3130 (4)	0·3699 (3)	−0·0730 (3)	0·0725
C(26)	0·3842 (4)	0·4004 (3)	−0·0014 (3)	0·0727
C(27)	0·3557 (3)	0·3866 (2)	0·0675 (2)	0·0549
C(28)	0·6634 (3)	0·3423 (2)	0·3872 (2)	0·0365
C(29)	0·6439 (3)	0·4271 (2)	0·4205 (2)	0·0411
C(30)	0·7226 (3)	0·4547 (3)	0·4921 (2)	0·0549
C(31)	0·7109 (4)	0·5349 (3)	0·5196 (2)	0·0705
C(32)	0·6231 (4)	0·5870 (3)	0·4759 (3)	0·0728
C(33)	0·5468 (4)	0·5612 (3)	0·4046 (3)	0·0625
C(34)	0·5567 (3)	0·4818 (2)	0·3769 (2)	0·0498
C(35)	0·6893 (3)	0·2709 (2)	0·4476 (2)	0·0390
C(36)	0·6634 (3)	0·2742 (3)	0·5184 (2)	0·0505
C(37)	0·6795 (4)	0·2053 (3)	0·5671 (2)	0·0630
C(38)	0·7189 (4)	0·1320 (3)	0·5443 (2)	0·0648
C(39)	0·7435 (4)	0·1273 (2)	0·4742 (2)	0·0567
C(40)	0·7291 (3)	0·1968 (2)	0·4259 (2)	0·0476
C(41)	0·7664 (3)	0·3600 (2)	0·3533 (2)	0·0384
C(42)	0·8828 (3)	0·3395 (2)	0·3950 (2)	0·0538
C(43)	0·9778 (3)	0·3636 (3)	0·3690 (3)	0·0630
C(44)	0·9573 (3)	0·4085 (3)	0·3003 (3)	0·0599
C(45)	0·8406 (4)	0·4310 (2)	0·2583 (2)	0·0579
C(46)	0·7458 (3)	0·4069 (2)	0·2838 (2)	0·0473

Table 2. *Atomic coordinates and isotropic thermal parameters for* (4)

U_{eq} is one third of the trace of the orthogonalized U_{ij} matrix. Atoms of the guest are C(47) through Cl(49).

	x	y	z	U_{eq}/U(Å²)
N(1)	0·2844 (8)	0·2432 (8)	−0·1671 (8)	0·0280
C(2)	0·1778 (10)	0·2416 (10)	−0·1487 (10)	0·0303
O(3)	0·0913 (8)	0·2015 (8)	−0·2207 (7)	0·0486
C(4)	0·1708 (10)	0·2959 (10)	−0·0297 (10)	0·0372
N(5)	0·2783 (8)	0·3000 (8)	0·0560 (8)	0·0309
C(6)	0·3692 (10)	0·3478 (10)	0·0354 (10)	0·0344
O(7)	0·4569 (8)	0·3989 (8)	0·1079 (8)	0·0529
C(8)	0·3621 (10)	0·3358 (10)	−0·0865 (10)	0·0378
C(9)	0·3017 (10)	0·1984 (10)	−0·2855 (9)	0·0333
C(10)	0·4222 (8)	0·1629 (8)	−0·2796 (6)	0·0381
C(11)	0·4812 (8)	0·1268 (8)	−0·1886 (6)	0·0498
C(12)	0·5842 (8)	0·0792 (8)	−0·1918 (6)	0·0597
C(13)	0·6282 (8)	0·0678 (8)	−0·2859 (6)	0·0658
C(14)	0·5692 (8)	0·1039 (8)	−0·3769 (6)	0·0525
C(15)	0·4662 (8)	0·1515 (8)	−0·3737 (6)	0·0437
C(16)	0·2307 (7)	0·0848 (7)	−0·3514 (5)	0·0338
C(17)	0·2153 (7)	0·0064 (7)	−0·2951 (5)	0·0413
C(18)	0·1649 (7)	−0·1020 (7)	−0·3576 (5)	0·0470
C(19)	0·1299 (7)	−0·1320 (7)	−0·4762 (5)	0·0501
C(20)	0·1452 (7)	−0·0535 (7)	−0·5325 (5)	0·0563
C(21)	0·1956 (7)	0·0549 (7)	−0·4700 (5)	0·0412
C(22)	0·2723 (6)	0·2953 (7)	−0·3390 (7)	0·0341
C(23)	0·1607 (6)	0·3045 (7)	−0·3947 (7)	0·0450
C(24)	0·1337 (6)	0·3979 (7)	−0·4338 (7)	0·0634
C(25)	0·2182 (6)	0·4822 (7)	−0·4170 (7)	0·0639
C(26)	0·3298 (6)	0·4729 (7)	−0·3612 (7)	0·0592
C(27)	0·3568 (6)	0·3795 (7)	−0·3222 (7)	0·0434
C(28)	0·2684 (10)	0·3097 (10)	0·1736 (9)	0·0349
C(29)	0·3829 (6)	0·2955 (6)	0·2521 (6)	0·0321
C(30)	0·4071 (6)	0·3511 (6)	0·3687 (6)	0·0380
C(31)	0·5043 (6)	0·3298 (6)	0·4420 (6)	0·0510
C(32)	0·5773 (6)	0·2530 (6)	0·3985 (6)	0·0566
C(33)	0·5531 (6)	0·1975 (6)	0·2818 (6)	0·0537
C(34)	0·4559 (6)	0·2187 (6)	0·2086 (6)	0·0430
C(35)	0·1951 (8)	0·2071 (8)	0·1706 (6)	0·0414
C(36)	0·1461 (8)	0·2157 (8)	0·2611 (6)	0·0541
C(37)	0·0862 (8)	0·1216 (8)	0·2660 (6)	0·0700
C(38)	0·0753 (8)	0·0188 (8)	0·1803 (6)	0·0747
C(39)	0·1243 (8)	0·0103 (8)	0·0897 (6)	0·0655
C(40)	0·1842 (8)	0·1044 (8)	0·0849 (6)	0·0486
C(41)	0·2203 (6)	0·4244 (8)	0·2144 (8)	0·0336
C(42)	0·2931 (6)	0·5230 (8)	0·2545 (8)	0·0491
C(43)	0·2492 (6)	0·6286 (8)	0·2777 (8)	0·0793
C(44)	0·1324 (6)	0·6356 (8)	0·2607 (8)	0·0862
C(45)	0·0595 (6)	0·5370 (8)	0·2206 (8)	0·0819
C(46)	0·1035 (6)	0·4314 (8)	0·1975 (8)	0·0611
C(47)	0·7154 (22)	0·3404 (22)	0·1009 (22)	0·152 (5)
Cl(48)	0·7504 (7)	0·3727 (7)	−0·0084 (7)	0·165 (3)
Cl(49)	0·8012 (8)	0·2481 (8)	0·1409 (8)	0·204 (4)

factor; the atomic coordinates were not refined. Least-squares calculations minimized $w(\Delta F)^2$ and were based on experimental weights $w = 1/\sigma^2(F_o)$ in (3) and on unit weights in (4). At convergence $\Delta/\sigma < 0{\cdot}2$. Final $R = 0{\cdot}047$, $wR = 0{\cdot}056$ for (3), $R = 0{\cdot}109$, $wR = 0{\cdot}109$ for (4). Final difference maps showed no indications of incorrectly placed or missing atoms; $\Delta\rho_{max}$ and $\Delta\rho_{min}$ respectively 0·33 and −0·21 e Å^{-3} in (3), and 0·40 and −0·62 e Å^{-3} in (4). Computations and illustrations performed with the following programs: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), an extensively modified version of *ORFLS* (Busing, Martin & Levy, 1962), *SHELX*76 (Sheldrick, 1976), *PARST* (Nardelli, 1983), *ORTEP*II (Johnson, 1976).* All calculations performed on CYBER 170-855 at Tel-Aviv University Computation Centre.

* Lists of structure factors, atomic parameters of the H atoms, anisotropic thermal parameters of the non-H atoms and covalent parameters within the phenyl rings in (3) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42318 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

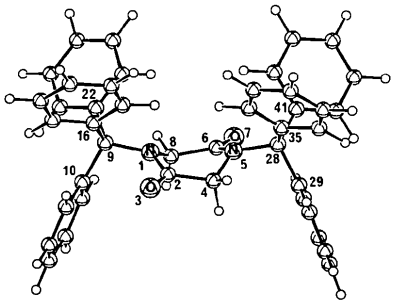

Fig. 1. Molecular structure of *N,N'*-dityril-2,5-diketopiperazine, showing the atom-numbering scheme.

Discussion. Tables 1 and 2 give atomic parameters for the two structures. Fig. 1 illustrates the molecular structure of *N,N'*-dityril-2,5-diketopiperazine as found in the crystals of the free compound; there are no significant variations in the overall geometry of this host in its complex with methylene chloride. The covalent bond lengths, angles and dihedral angles obtained for the two compounds are compared in Table 3. Most of the individual parameters have similar values in the two structures, exhibiting no extraordinary features; however, in (4) they are significantly less reliable (see *Experimental*).

The molecular framework of the substituted diketopiperazine is characterized by an approximate C_2 symmetry. The central six-membered ring is folded about an axis passing through the two methylene C atoms, the dihedral angle between the two (−NCOCH$_2$−) halves of the ring being 30·6 (2)° in (3) and 28 (1)° in (4). The methylene C atoms lie 0·286–0·289 (3) Å in (3) and 0·283–0·294 (9) Å in (4) below the mean plane of this ring, while the N atoms lie 0·316–0·319 (3) and 0·291–0·303 (8) Å in (4) above it. The N–C(Tr) bonds are equatorial to the ring. A similar deviation from planarity of the diketopiperazine moiety has been observed in the crystal structure of L-*cis*-3,6-dimethyl-2,5-diketopiperazine where the angle between the mean planes of the two amide groups is 26° (Benedetti, Corradini & Pedone, 1969*a*). On the other hand, in the *trans* isomer of the above compound (Benedetti, Corradini & Pedone, 1969*b*) as well as in *N,N'*-dimethyldiketopiperazine (Groth, 1969) and in the unsubstituted diketopiperazine (Degeilh & Marsh, 1959) the six-membered ring was found to be essentially planar. It appears that intra- and intermolecular van der Waals forces play an important role in determining the different conformations of the piperazine rings in the respective crystals (Benedetti, Corradini, Goodman & Pedone, 1969). The steric strain in the present structure

Table 3. *Bond distances* (Å), *bond angles* (°) *and dihedral angles* (°) *for* (3) *and* (4) *with e.s.d.'s in parentheses*

	(3)	(4)		(3)	(4)		(3)	(4)
N(1)–C(2)	1·364 (5)	1·37 (2)	C(6)–C(8)	1·506 (4)	1·49 (2)	C(28) N(5)	1·495 (4)	1·49 (2)
C(2)–O(3)	1·233 (5)	1·21 (1)	C(8)–N(1)	1·462 (5)	1·45 (1)	C(28) C(29)	1·541 (5)	1·55 (1)
C(2)–C(4)	1·497 (4)	1·49 (2)	C(9)–N(1)	1·499 (4)	1·51 (1)	C(28)–C(35)	1·538 (5)	1·53 (2)
C(4)–N(5)	1·466 (5)	1·48 (1)	C(9)–C(10)	1·540 (5)	1·53 (2)	C(28)–C(41)	1·538 (5)	1·54 (2)
N(5)–C(6)	1·367 (4)	1·37 (2)	C(9)–C(16)	1·538 (5)	1·54 (1)	C(47)–Cl(48)	—	1·69 (3)
C(6) O(7)	1·218 (5)	1·25 (1)	C(9)–C(22)	1·542 (5)	1·54 (2)	C(47)–Cl(49)	—	1·66 (3)
C(2)–N(1)–C(8)	113·0 (3)	114 (1)	C(6)–N(5)–C(28)	124·3 (3)	123 (1)	C(10)–C(9) C(22)	103·0 (3)	115 (1)
C(2)–N(1)–C(9)	120·6 (3)	121 (1)	N(5)–C(6)–O(7)	126·4 (3)	127 (1)	C(16) C(9)–C(22)	113·6 (3)	115 (1)
C(8)–N(1)–C(9)	119·4 (3)	118 (1)	N(5)–C(6)–C(8)	114·4 (3)	116 (1)	N(5) C(28) C(29)	107·9 (3)	112 (1)
N(1)–C(2)–O(3)	125·8 (3)	126 (1)	O(7)–C(6)–C(8)	119·1 (3)	118 (1)	N(5)–C(28)–C(35)	105·5 (3)	110 (1)
N(1)–C(2)–C(4)	115·4 (3)	116 (1)	C(6)–C(8) N(1)	114·0 (3)	115 (1)	N(5) C(28) C(41)	112·2 (3)	105 (1)
O(3)–C(2) C(4)	118·6 (3)	119 (1)	N(1)–C(9) C(10)	110·0 (3)	110 (1)	C(29) C(28) C(35)	115·2 (3)	101 (1)
C(2)–C(4)–N(5)	113·6 (3)	113 (1)	N(1)–C(9)–C(16)	106·6 (3)	111 (1)	C(29) C(28) C(41)	102·3 (3)	114 (1)
C(4) N(5)–C(6)	113·8 (3)	114 (1)	N(1)–C(9)–C(22)	109·1 (3)	105 (1)	C(35) C(28)–C(41)	113·8 (3)	115 (1)
C(4) N(5)–C(28)	114·7 (3)	116 (1)	C(10)–C(9)–C(16)	114·5 (3)	101 (1)	Cl(48)–C(47)–Cl(49)	—	109 (2)
N(1)–C(2) C(4) N(5)	20·1 (4)	24 (2)	C(4)–N(5)–C(6) C(8)	30·7 (4)	29 (2)	C(6) C(8)–N(1)–C(2)	54·4 (4)	−51 (1)
C(2) C(4) N(5) C(6)	53·5 (4)	53 (1)	N(5)–C(6)–C(8)–N(1)	21·2 (4)	22 (2)	C(8)–N(1) C(2)–C(4)	31·5 (4)	26 (1)

Within the aromatic rings [atoms C(10) through C(27) and C(29) through C(46)]: In (3) the bond lengths and angles calculated from the freely refined coordinates are within 1·363 (6)–1·410 (6) Å and 117·7 (3)–123·4 (3)° (see supplementary material). In (4) the C–C bonds and C–C C angles were constrained to 1·395 Å and 120·0° respectively.

can be appreciated by inspecting the short intramolecular nonbonding distances between the central fragment and the peripheral trityl groups. For example, in (3) the relevant distances O(3)···C(10) = 2·877 (4); O(7)···C(41) = 2·822 (4); C(4)···C(29) = 2·959 (5); C(4)···C(35) = 2·904 (4); C(18)···C(22) = 2·922 (4) Å are considerably shorter than the corresponding sums of van der Waals radii. Similarly short distances are present in (4). The characteristic twist between the phenyl rings in each trityl substituent can be described in terms of dihedral angles formed between these planes. The corresponding sets of data are: 59·1 (1), 59·9 (1), 87·2 (1)° and 56·2 (1), 65·5 (1), 88·7 (1)° in (3), and 58·6 (4), 65·4 (4), 85·3 (4)° and 60·7 (4), 63·0 (4), 89·8 (4)° in (4).

Another aspect of the molecular structure deserves particular attention as it has a direct influence on the packing modes observed in the two crystals. In the observed conformation, four phenyl groups are located 'above' the mean plane of the diketopiperazine core and two phenyl groups 'below' it (Fig. 1). The former have their planes roughly parallel to the N···N axis, their H atoms essentially covering the nitrogen side of the ring. There is more empty space on the opposite side of this ring where the two 'lower' phenyls are roughly parallel to the axial C—H bonds of the methylene groups. In the crystalline phase where a close packing of the molecules is required, such space on the molecular surface can be occupied in two different manners; either by suitable fragments of an adjacent molecule or by other molecules which during the process of crystallization are carried out from the solution into the lattice. An illustration of these features is provided by the crystal structures (3) and (4).

Stereoviews of the packing arrangement of the free host and of its inclusion complex with methylene chloride are shown in Figs. 2 and 3 respectively. In both structures the *N,N'*-ditrityldiketopiperazine molecules are aligned with their N···N axes parallel to each other. However, in (3) there is a translational shift between adjacent molecules in such a manner that a phenyl ring of one molecule can approach the open side above the central part of another molecule and that the large trityl end groups can pack efficiently. The corresponding shortest intermolecular distances in this structure are O···C(aryl) = 3·41 Å and C(aryl)···C(aryl) = 3·53 Å. In the crystal structure of (4) all host molecules have the same orientation and their centers positioned very close to the *ab* plane of the unit cell [approximately at (0·28, 0·27, −0·05) and (0·72, 0·73, 0·05)]. In every layer of host molecules on a single *ab* plane the trityl groups of neighboring species are located within van der Waals contacts next to each other. It can clearly be seen that the space around the central part of the host is now occupied by smaller guest molecules of methylene chloride. In the resulting structure (Fig. 3) every guest moiety is within pseudo-cage-type voids surrounded by four adjacent hosts. The rather large-amplitude thermal motion (possible translational and rotational disorder) of the guest molecules in the lattice is consistent with the observation that there are no specific interactions between the two component entities, all intermolecular distances being equal to or larger than the sums of the corresponding van der Waals radii.

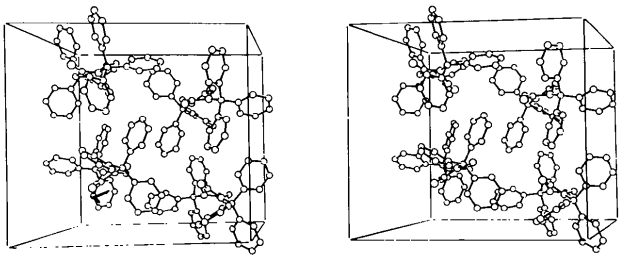

Fig. 2. Stereoview of the crystal structure of *N,N'*-ditrityl-2,5-diketopiperazine, approximately down **a**.

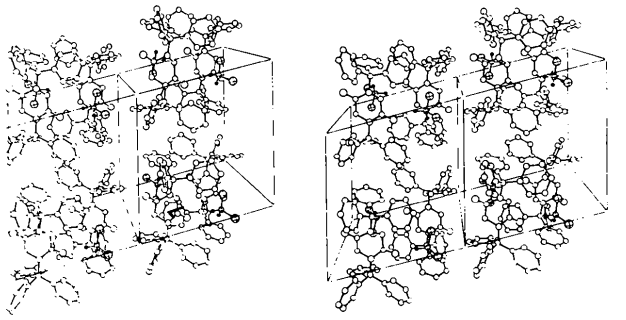

Fig. 3. Stereoview of the crystalline 1:1 inclusion complex of *N,N'*-ditrityl-2,5-diketopiperazine with methylene chloride.

The above data supplement and are in agreement with the results of our previous studies of molecular design for hosts that can form crystalline host–guest complexes with neutral guests.

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3-(4-Carbamoylphenyl)-1-methyltriazene 1-Oxide

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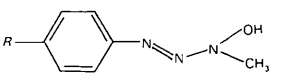
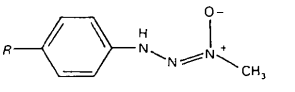
Abstract. $C_8H_{10}N_4O_2$, $M_r = 194{\cdot}19$, $P2_1/a$, $a = 9{\cdot}708$ (2), $b = 6{\cdot}7806$ (5), $c = 14{\cdot}707$ (2) Å, $\beta = 101{\cdot}30$ (1)°, $V = 949{\cdot}3$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}359$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 8{\cdot}137$ cm^{-1}, $F(000) = 408$, $T = 298$ K, $R = 0{\cdot}037$ for 1028 unique significant reflections. The molecule adopts the *N*-oxide rather than the *N*-hydroxyl form in agreement with the spectroscopic evidence. The atoms of the triazene *N*-oxide group are planar with the oxygen atom *cis* to N(1) of triazene. The atoms of the amide group are also planar. The amide hydrogen atoms are involved in hydrogen bonding.

Introduction. Aryldialkyltriazenes have generated considerable interest as second-generation analogues of the clinically used anti-tumour agent 5-(3,3-dimethyl-1-triazeno)imidazole-4-carboxamide (Wilman & Farmer, 1985). In establishing the structural requirements for anti-tumour activity of this class of compounds, we investigated 3-(4-carbamoylphenyl)-1-methyltriazene 1-oxide [(I*b*), $R = -CONH_2$: CB10-339 (Connors, Goddard, Merai, Ross & Wilman, 1976)] and showed it to be active against the TLX/5 lymphoma and the AdjPC6/A plasmacytoma (Wilman, 1985). It has also been reported as having immunosuppressive activity (Hess, Stewart, Possanza & Freter, 1974).

Compounds of this type are commonly synthesized by the reaction of an aryldiazonium salt with *N*-methylhydroxylamine, and were originally described as 1-aryl-3-hydroxy-3-methyltriazenes (I*a*). However, infrared (Mitsuhashi, Osamura & Shimamura, 1965) and ^{1}H and ^{13}C NMR data (Giumanini, Lassiani, Nisi, Petric & Stanovnik, 1983) tend to suggest that the structure is better described as a 3-aryl-1-methyltriazene 1-oxide (I*b*). As the structural variation will have a considerable effect on the potential of these compounds for metabolism, a necessary prerequisite for anti-tumour activity, we have been prompted to establish the structure conclusively.



(I*a*)



(I*b*)

Experimental. Colourless elongated crystals obtained from ethanol solution, which proved to be twin crystals possessing common *b* and *c* axes. Data collection and structure determination carried out, initially, with a twin crystal and later with a single crystal obtained from acetone solution. Single crystal employed for data collection had dimensions 0·10 × 0·06 × 0·06 mm.

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