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Crystal Structures of 1, 5-Diacetyl-2, 2, 4-trimethyl-1H-tetrahydro-1, 5-benzodiazepine (DARTMBD) and N_5-Ethoxycarbonyl-2-methyl-2, 4-diphenyl-1H-tetrahydro-1, 5-benzodiazepine (ECRPMBD)

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Crystal Structures of 1, 5-Diacetyl-2, 2, 4-trimethyl-1H-tetrahydro-1, 5-benzodiazepine (DARTMBD) and N_5-Ethoxycarbonyl-2-methyl-2, 4-diphenyl-1*H*-tetrahydro-1, 5-benzodiazepine (ECRPMBD)

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The benzodiazepines, namely 1, 5-Diacetyl-2, 2, 4-trimethyl-1H-tetrahydro-1, 5-benzodiazepine ($C_{16}H_{22}N_2O_2$), (DARTMBD, CCDC 716181) and N_5*-Ethoxycarbonyl-2-methyl-2, 4-diphenyl-1*H*-tetrahydro-1, 5-benzodiazepine ($C_{25}H_{26}N_2O_2$), (ECRPMBD, CCDC 716182) possess potential pharmacological activities. DARTMBD crystallizes in monoclinic space group $P2_1/c$ with cell parameters:* a = *10.0582(3) Å,* b = *9.6019(3)* °, c = *16.0837(4)* °, β = *103.100(1)*°, *and* V = *1512.91(8)* °^{3}*; ECRPMBD crystallizes in triclinic system, P*$\bar{1}$ *with two crystallographically independent molecules in the asymmetric unit. The cell parameters are:* a = *12.2807(4)* °, b = *12.8410(5)* °, c = *13.9714(4)* °, α = *90.626(2)*°, β = *105.200(3)*°, γ = *100.324(2)*°, *and* V = *2087.84(12)*°^{3}*. Both the structures were solved by direct methods and refined by full-matrix least-squares procedures to final* R*-values of 0.0552 and 0.0487, respectively. The benzodiazepine ring in both the structures adopts twist-boat conformation. In DARTMBD, the dimer formation occurs through C–H. . .O intermolecular interactions whereas in ECRPMBD, the molecules are stabilized by N–H. . .O, and C–H. . .O types of hydrogen bonds.*

Keywords Benzodiazepines; conformation; crystal structure; hydrogen bonding

Introduction

The benzo derivatives of azepines constitute a widely prescribed class of psychoactive drugs. Benzodiazepines are known for their natural occurrence in filamentous fungi and actinomycetes of the *genera pencillium*, *aspergillus, and streptomyces* [1]. These benzodiazepines are widely used as antipyretic [2], antianxiety [3], and hypnotic agents [4]. The 1, 5-Benzodiazepines are valuable synthons used for the synthesis of new heterocyclic compounds, such as benzimidazole, isoxazole and pyrazole [5–7]. The importance of 1, 5-benzodiazepines is evident from the pharmaceutical applications of clobazam [8].

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Experimental

Synthesis

DARTMBD. To an ice-cold solution of tetrahydrobenzodiazepine (0.95 g, 5 mmol) in anhydrous benzene (25 mL), triethylamine (2 mL, 15 mmol), and acetyl chloride (1.28 g, 15 mmol) were added. The reaction mixture was stirred at room temperature for 2 h. The precipitated ammonium salt was filtered off and the filtrate was washed with water (4 × 20 mL). The benzene solution was dried over anhydrous Na_2SO_4 and concentrated after passing through a short column of silica. The resulting solid was purified by using benzene to yield pale yellowish brown crystals, m.p. 199°C–200°C. The analytical data are: $C_{16}H_{22}N_2O_2$ Calculated: C, 70.04; H, 8.09; N, 10.31%. Found: C, 70.26; H, 8.41; N, 10.02% [9]. The schematic preparation of the sample is shown in Fig. 1(a).

ECRPMBD. To a solution of 1, 2-diaminobenzene (100 mmol) in glacial acetic acid (50 mL), acetophenone (200 mmol) was added while shaking and kept stirred at 25°C for 6 h. The reaction mixture was then poured into crushed ice and basified with ammonia solution. The precipitated solid was separated, washed thoroughly with water and dried. To a stirred solution of benzodiazepine (10 mmol) in methanol (200 mL), sodiumborohydride (20 mmol) was added in seven portions for a period of 3 h. The temperature of the reaction mixture was maintained at 40°C using a water bath. After the completion of the reaction, the solution was concentrated and left undisturbed for a day. To the solution (5 mmol) in benzene (30 mL) was added triethylamine (10 mmol), and ethylchloroformate (10 mmol) and kept at the room temperature for 20 h. The resulting compound was purified by recrystallization from ethanol and pet-ether (60ºC–80ºC). m.p. 94ºC–96°C. The purity of the compound was confirmed using TLC before using it for growing single crystals by slow evaporation method. In addition, the recrystallization was repeated to get a constant melting point that in turn confirms the purity of the synthesized compound ECRPMBD. IR Spectrum: 3377 cm^{-1} (N_2-H stretching) and 1693 cm^{-1} (N_5–C=O, amide carbonyl stretching) confirms the formation of the compound. Mass: m/e: 386 [M+ ion]. The purity of the compound was confirmed by CHN analysis. The analytical data are: $C_{25}H_{26}N_2O_2$– Calculated: C, 77.69; H, 6.78; N, 7.25%. Found: C, 77.45; H, 6.91; N, 7.08%. The schematic preparation of the sample is shown in Fig. 1(b).

Data Collection

Colorless transparent crystals of DARTMBD and ECRPMBD of dimensions 0.15 × 0.15 × 0.20 mm and 0.16 × 0.17 × 0.16 mm were chosen for intensity data collection in a Bruker axs kappa Apex II single crystal X-ray diffractometer equipped with graphite monochromated Mo(Kα) ($\lambda = 0.7107$ Å) radiation [10] and CCD detector. The unit cell parameters were determined from 36 frames (0.5° phi-scan) measured from three different crystallographic zones and using the method of difference vectors. The intensity data were collected with an average four-fold redundancy per reflection and optimum resolution (0.75 Å). The intensity data collections were processed by applying Lorentz and polarization (Lp) correction and decay correction by using the program SAINT-NT (version 6.0). Empirical absorption correction (multi-scan) was performed using SADABS program [11].

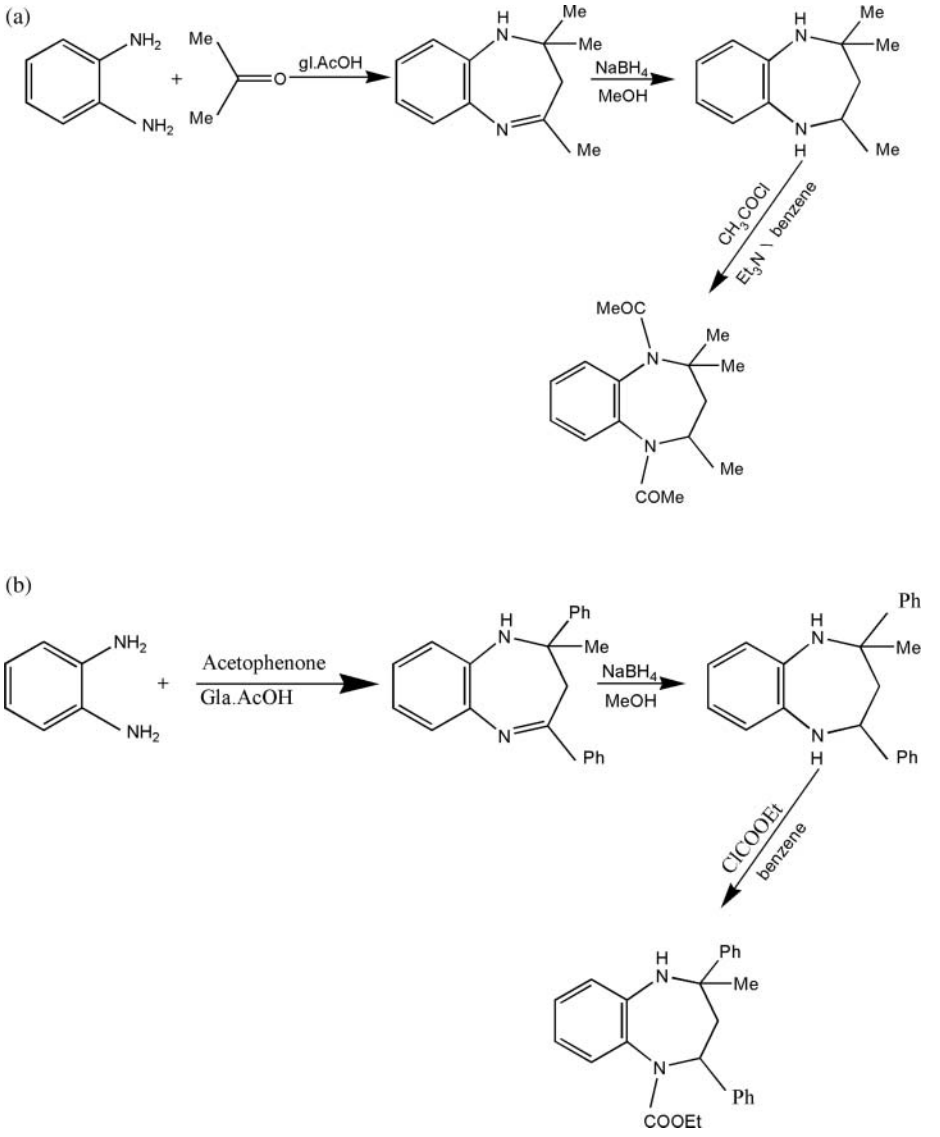

Figure 1. (a) The schematic preparation of DARTMBD. **(b).** The schematic preparation of ECRPMBD.

Structure Solution

The structures were solved by direct methods using the program SHELXS97 [12] and refined on F^2 by full-matrix least-squares procedures using the program SHELXL97 [13]. The nonhydrogen atoms were refined anisotropically and the hydrogen atoms in both the structures were constrained to ride on their respective parent atoms. The final cycle of refinement converged to $R_1 = 0.0552$ and 0.0487 for the molecules DARTMBD and ECRPMBD, respectively. The geometrical parameters and the figures were done using the programs PARST [14] and PLATON [15]. The crystal data and other relevant

Table 1. Crystal data for DARTMBD and ECRPMBD

Parameters	DARTMBD	ECRPMBD
CCDC	716,181	716,182
Empirical formula	C_{16} H_{22} N_2 O_2	C_{25} H_{26} N_2 O_2
Formula weight	274.36	386.48
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a(Å)	10.0582(3)	12.2807(4)
b(Å)	9.6019(3)	12.8410(5)
c(Å)	16.0837(4)	13.9714(4)
$\alpha(^\circ)$		90.626(2)
$\beta(^\circ)$	103.100(1)	105.200(3)
$\gamma(^\circ)$		100.324(2)
Volume (Å^3)	1512.91(8)	2087.84(12)
Z	4	4
Calculated density (Mg m^{-3})	1.205	1.230
Absorption coefficient (mm^{-1})	0.080	0.078
F (000)	592	824
Crystal size (mm)	0.15 × 0.15 × 0.20	0.16 × 0.17 × 0.16
θ – range for data collection	2.49° to 33.81°	1.61° to 25.50°
Limiting indices	–15 <= h <= 15 –14 <= k <= 15 –18 <=l<= 25	–14 <= h <= 14 –15 <= k <= 15 –16 <= l <= 16
Reflections collected/unique	22,352/5982 [R(int) = 0.0302]	41,612/7698 [R(int) = 0.0327]
Completeness to $\theta = 25.00$	100.00%	99.90%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5982/0/183	7698/2/532
Goodness-of-fit on F^2	1.018	1.018
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0552$, $wR_2 = 0.1495$	$R_1 = 0.0486$, $wR_2 = 0.1303$
R indices (all data)	$R_1 = 0.0980$, $wR_2 = 0.1755$	$R_1 = 0.0822$, $wR_2 = 0.1534$
Extinction coefficient	–	0.0076(12)
Largest diff. peak and hole (eÅ^{-3})	0.389 and –0.158	0.232 and –0.254

Table 2(a). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) involving nonhydrogen atoms for DARTMBD

Atom	x	y	z	*U (eq)
O1	2849(1)	715(1)	–873(1)	62(1)
O2	918(1)	234(1)	2342(1)	58(1)
N1	3025(1)	2160(1)	251(1)	32(1)
C2	4382(1)	1598(1)	668(1)	35(1)
C3	4578(1)	1608(1)	1638(1)	36(1)
C4	3463(1)	928(1)	2011(1)	36(1)
N5	2165(1)	1761(1)	1754(1)	32(1)
C6	2231(1)	3141(1)	1436(1)	29(1)
C7	2583(1)	3339(1)	651(1)	29(1)
C8	2588(1)	4672(1)	320(1)	38(1)
C9	2246(2)	5803(1)	759(1)	44(1)
C10	1942(2)	5614(1)	1545(1)	42(1)
C11	1949(1)	4292(1)	1890(1)	37(1)
C12	2346(2)	1628(1)	–512(1)	41(1)
C13	952(2)	2196(2)	–883(1)	60(1)
C14	5503(2)	2412(2)	391(1)	53(1)
C15	3229(2)	–567(1)	1669(1)	55(1)
C16	3935(2)	951(2)	2986(1)	57(1)
C17	967(1)	1289(1)	1923(1)	40(1)
C18	–328(2)	2070(2)	1546(1)	54(1)

*U (eq) = $(1/3)\sum_i\sum_j U_{ij} a_i \times a_j \times a_i.a_j$.

parameters are given in Table 1. The atomic coordinates with their equivalent isotropic displacement factors for non-hydrogen atoms are presented in Tables 2(a) and (b), respectively.

Results and Discussion

The ORTEP plots of the molecules DARTMBD and ECRPMBD (molecules A and molecules B) are shown in Figs 2(a) and (b). The fragment N1-C7-C6-N5 in the seven-membered ring is conjugated with the adjacent benzene ring in both DARTMBD and ECRPMBD molecules.

The analysis based on spectroscopic data and semi-empirical calculations suggest that the diazepine rings normally adopt chair, boat, or twist-boat conformation depending on the flipping of N1–C7–C6–N5 angle in the molecule [9, 16]. The crystallographic study on asymmetry parameters, torsion angles, and least-squares planes reveal that the diazepine ring in both the structures adopts twist-boat confirmation [$q(2) = 1.0658(12)$ Å, $q(3) = 0.0554(12)$ Å, $\varphi(2) = 163.81(6)^\circ$, $Q_T = 1.067(1)$ for DARTMBD and $q(2) = 0.9803(20)$ Å, $q(3) = 0.0921(22)$ Å, $\varphi(2) = 155.05(12)^\circ$, $Q_T = 0.985(2)$ and $q(2) = 0.9735(20)$ Å, $q(3) = 0.0964(20)$ Å, $\varphi(2) = 154.73(11)^\circ$, $Q_T = 0.978(2)$ for molecules A and B of

Table 2(b). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) involving nonhydrogen atoms for ECRPMBD

	Molecule A				Molecule B			
Atom	x	y	z	*U (eq)	x	y	z	*U (eq)
O1	1522(2)	9740(2)	3218(2)	92(1)	8438(2)	5240(2)	9781(2)	116(1)
O2	2243(1)	8861(1)	4551(1)	79(1)	7795(2)	6157(2)	10,824(2)	104(1)
N1	5330(2)	9735(1)	3956(1)	57(1)	4604(2)	5331(2)	8796(1)	61(1)
C2	5264(2)	10,120(2)	2952(1)	48(1)	4664(2)	4922(2)	7825(1)	50(1)
C3	4295(2)	9410(2)	2174(1)	49(1)	5656(2)	5595(2)	7511(1)	49(1)
C4	3090(2)	9340(2)	2290(1)	52(1)	6852(2)	5626(2)	8183(2)	57(1)
N5	2995(1)	8903(1)	3242(1)	56(1)	6963(1)	6082(1)	9185(1)	62(1)
C6	3759(2)	8251(2)	3752(2)	53(1)	6231(2)	6766(2)	9355(1)	59(1)
C7	4924(2)	8691(2)	4121(1)	51(1)	5053(2)	6371(2)	9173(1)	57(1)
C8	5628(2)	8080(2)	4714(2)	66(1)	4378(2)	7016(2)	9447(2)	76(1)
C9	5199(3)	7072(2)	4916(2)	81(1)	4849(4)	8023(3)	9867(2)	99(1)
C10	4071(3)	6631(2)	4519(2)	82(1)	5996(4)	8418(2)	10,010(2)	103(1)
C11	3349(2)	7221(2)	3934(2)	69(1)	6680(3)	7793(2)	9748(2)	82(1)
C12	6378(2)	10,069(2)	2673(1)	51(1)	3576(2)	4999(2)	7014(1)	51(1)
C13	6929(2)	10,885(2)	2238(2)	69(1)	3043(2)	4208(2)	6282(2)	74(1)
C14	7932(2)	10,798(3)	1990(2)	93(1)	2101(2)	4328(3)	5533(2)	95(1)
C15	8393(2)	9914(3)	2162(2)	95(1)	1669(2)	5238(3)	5497(2)	92(1)
C16	7835(2)	9086(3)	2567(2)	87(1)	2183(2)	6038(2)	6213(2)	81(1)
C17	6848(2)	9164(2)	2819(2)	67(1)	3124(2)	5918(2)	6959(2)	65(1)
C18	5043(2)	11247(2)	2988(2)	64(1)	4836(2)	3780(2)	7955(2)	69(1)
C19	2195(2)	8731(2)	1413(2)	57(1)	7772(2)	6193(2)	7739(2)	57(1)
C20	2186(2)	7704(2)	1143(2)	80(1)	7841(2)	7238(2)	7516(2)	72(1)
C21	1354(3)	7181(2)	329(2)	95(1)	8704(2)	7740(2)	7123(2)	83(1)
C22	537(3)	7674(3)	–213(2)	97(1)	9495(2)	7191(3)	6948(2)	85(1)
C23	547(3)	8684(3)	38(2)	111(1)	9433(2)	6164(3)	7154(2)	84(1)
C24	1368(2)	9216(2)	845(2)	88(1)	8580(2)	5663(2)	7549(2)	69(1)
C25	2195(2)	9210(2)	3635(2)	64(1)	7794(2)	5789(2)	9926(2)	80(1)
C26	1348(2)	9085(3)	4984(2)	95(1)	8687(3)	5883(3)	11,637(3)	150(2)
C27	307(2)	8271(3)	4633(2)	113(1)	9484(3)	6740(3)	12,095(3)	152(2)

*U (eq) = $(1/3)\sum_i\sum_j U_{ij} a_i \times a_j \times a_i.a_j$.

ECRPMBD, respectively]. The sum of the bond angles around the hetero nitrogen atom in both structures [359.4° and 359.7° in DARTMBD and 359.9° and 357.9° for molecule A and 348.6° and 360° for molecule B of ECRPMBD] show that the atom N is in sp^2 hybridized state. The hetero π – electrons over N–C=O moiety observed in both the structures reveal the delocalization effect that is evident from the bond lengths (N1–C12=) 1.362(2) Å, (N5–C17=) 1.372(2) Å in DARTMBD and (N5–C25=) 1.357(3) Å, 1.359(3)Å (in molecules A and B) of ECRPMBD. The diazepine ring orients at an angle of 57.22(4)°

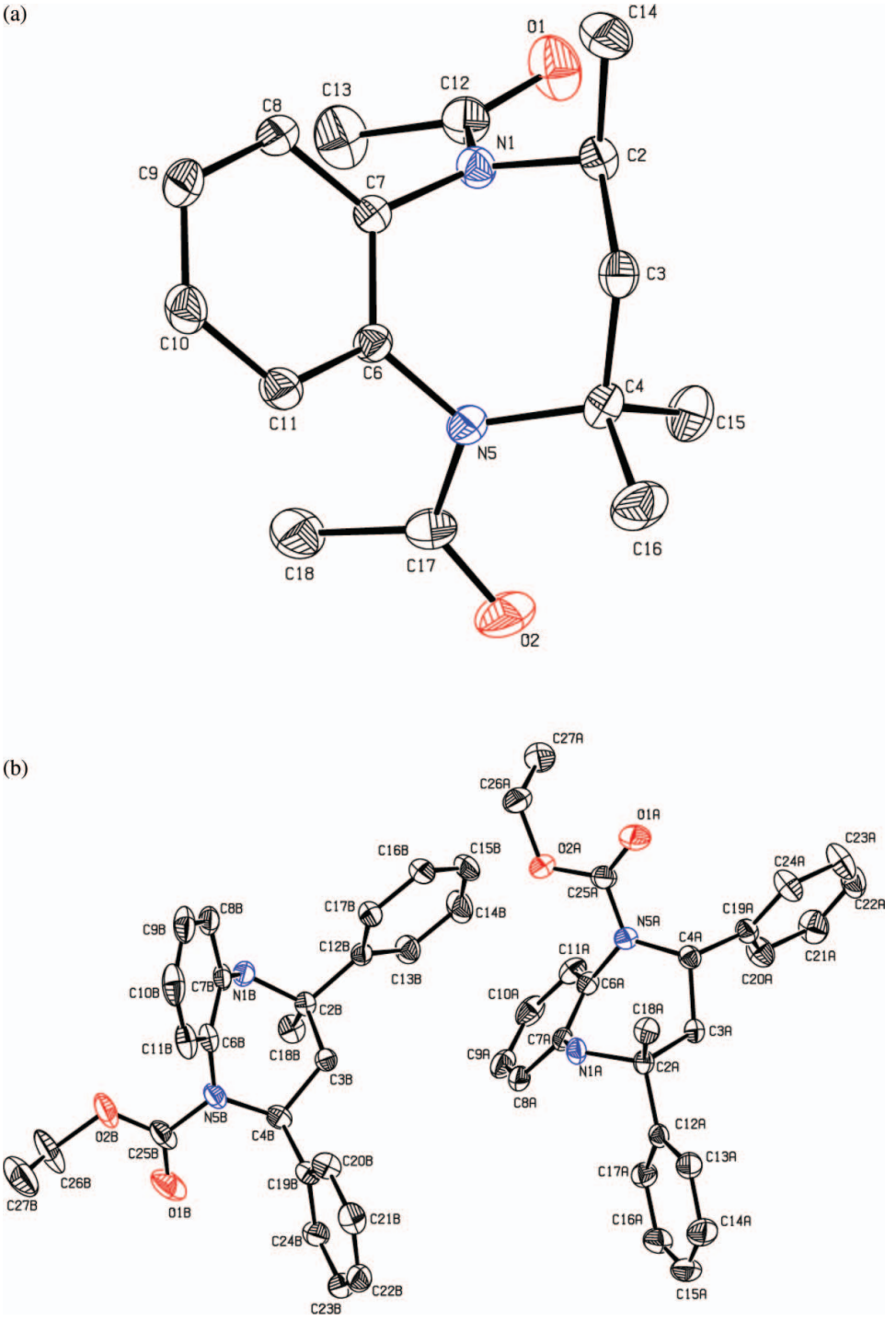

Figure 2. **(a)** The ORTEP plot of DARTMBD. **(b)** The ORTEP plot of ECRPMBD (molecules A and B).

Table 3. Hydrogen bonding geometry (Å and °) for DARTMBD and ECRPMBD

	D–H . . . A	d(D–H)	d(H . . . A)	d(D . . . A)	∠(DHA)
DARTMBD	C13–H13C . . . O2^{i}	0.960	2.5742	3.534(2)	178.1(1)
ECRPMBD	C21A–H21A . . . O1B^{i}	0.930	2.268	3.169(4)	163
	N1A–H1A . . . O2A^{ii}	0.853(2)	2.512(2)	3.349(2)	167.3(2)
	C21B–H21B . . . O1A^{ii}	0.930	2.417	3.327(4)	166.1
	N1B–H1B . . . O2B^{iii}	0.841(3)	2.571(3)	3.381(3)	162.2(3)
	C18B–H18E . . . Cg1^{iv}	0.9600	3.0642	4.008(3)	167.9
	C18A–H18B . . . Cg2^{v}	0.9600	3.0317	3.980(2)	169.6
	C26A–H26B . . . Cg3^{v}	0.9600	2.7498	3.658(3)	156.2
	C26B–H26C . . . Cg4^{vi}	0.9600	2.8849	3.842(4)	169.2
	C27B–H27F . . . Cg5^{vii}	0.9600	2.8426	3.785(4)	167.1
	C22A–H22A . . . Cg6^{viii}	0.9600	2.7611	3.659(3)	162.7

DARTMBD: Symmetry codes. (i) –x ,–y. –z
ECRPMBD: *Symmetry codes*. (i) –x + 1, –y + 1, –z + 1 (ii) –x + 1, –y + 2, –z + 1 (iii) –x + 1, –y + 1,–z + 2
(iv) 1 – x, 1 –y , 1 – z (v) 1 –x , –y, 1 – z (vi) 1 – x, 1 – y, –z (vii) –1 + x, y, –1 + z
(viii) 1 + x, y, 1 + z
Cg1 denotes centroid of ring C6A–C11A
Cg2 denotes centroid of ring C6B–C11B
Cg3 denotes centroid of ring C12A–C17A
Cg4 denotes centroid of ring C12B–C17B
Cg5 denotes centroid of ring C19A–C24A
Cg6 denotes centroid of ring C19B–C24B

with respect to the benzene in DARTMBD and 22.4(1)° and 22.3(1)° (for molecules A and B) in ECRPMBD, respectively.

The phenyl rings are planar and axially oriented with respect to the diazepine ring substituted at the 2nd and 4th positions in ECRPMBD [C7A–N1A–C2A–C12A=] –93.6(2)°; [C7B–N1B–C2B–C12B =] –93.8(2)°; [C6A–N5A–C4A–C19A =] 102.1(2)°; [C6B–N5B–C4B–C19B =] 102.9(2)°. The methyl groups adjoining C2 atoms [C7A–N1A–C2A–C12A = 144.5(2)°; C7B–N1B–C2B–C12B = 144(2)°] are in equatorial orientation.

In DARTMBD, the methyl groups at C2 and C4 assume [C7–N1–C2–C14 = –83.12°; C6–N5–C4–C16 = 101.72°] axial orientation whereas the one at C15 is in equatorial orientation [C6–N5–C4–C15 = –135.75°].

The packing of the molecules viewed down a-axis in both the molecules is shown in Figures 3(a) and (b). In DARTMBD, an intermolecular C–H . . . O hydrogen bond (Table 3) stabilizes the structure in addition to van der Waals forces. Dimerization between the molecules is formed through the atom C13 and O2 (–x, –y, –z), which leads to the ring pattern of $R_2^2(20)$ [17].

In ECRPMBD, the molecules are stabilized by N–H . . . O and C–H . . . O types of hydrogen bonds in addition to van der Waals forces. The N–H . . . O intermolecular hydrogen bonds (Table 3) are formed between the symmetry related molecules resulting in the formation of a network of dimeric structures with a ring pattern of $R_2^2(20)$ [17]. The molecules in the crystal structure form a chain along c-axis via C–H . . . O intermolecular interactions.

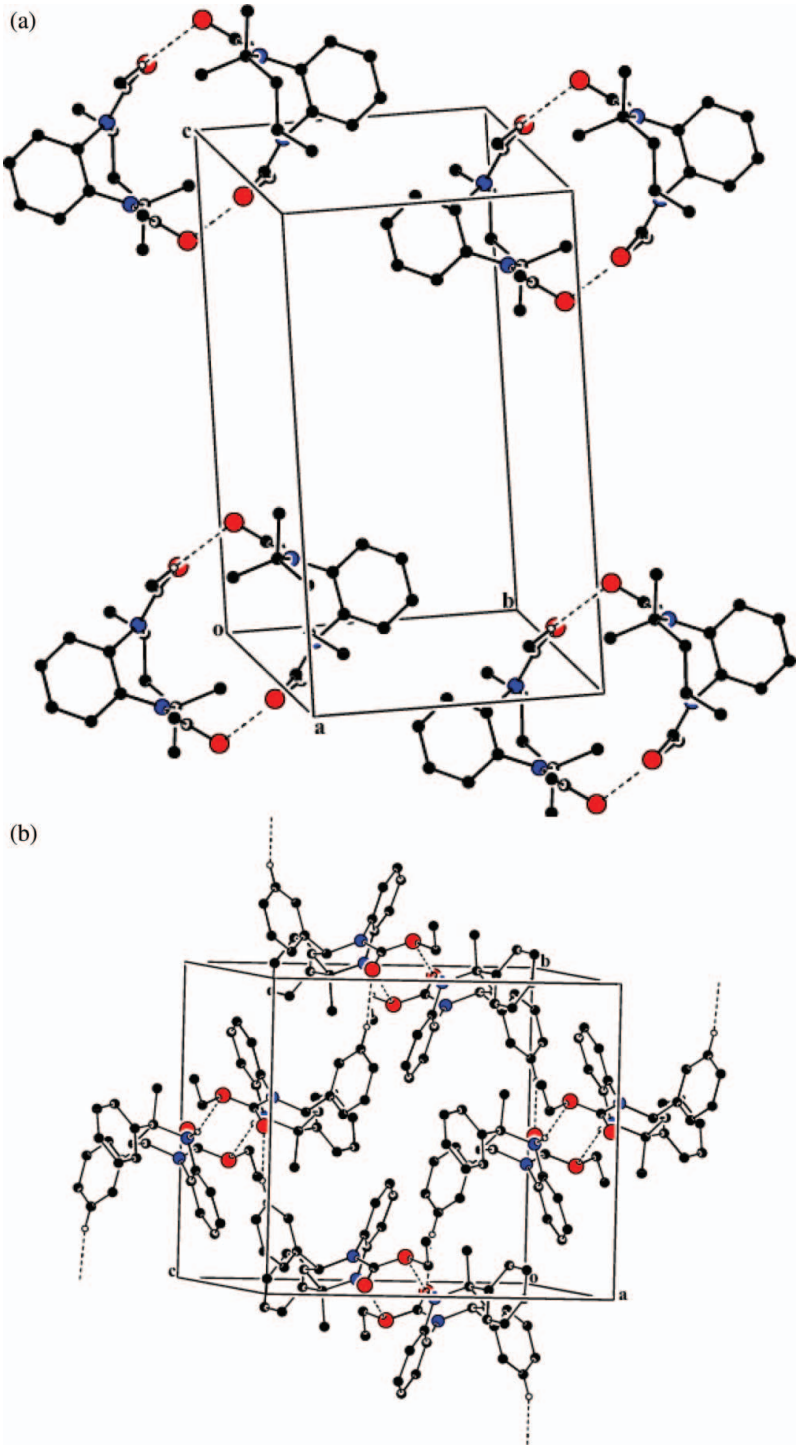

Figure 3. **(a)** Packing of DARTMBD molecules viewed down a-axis showing the dimer formation through C–H . . . O interactions. **(b).** Packing of the ECRPMBD molecules viewed down the a-axis.

Abbreviations

CCDC	Cambridge Crystallographic Data Centre
TLC	Thin Layer Chromotography
IR	Infrared Spectrum
CHN	Carbon–Hydrogen–Nitrogen
CCD Detector	Charge Coupled Device Detector

SHELX, PARST, and PLATON are the standard crystallographic software programs used.

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