Chemical Reactions in the Solid State. Part 1. Photochemical Dimerization of 1-Methyl-5,6-diphenylpyrazin-2-one

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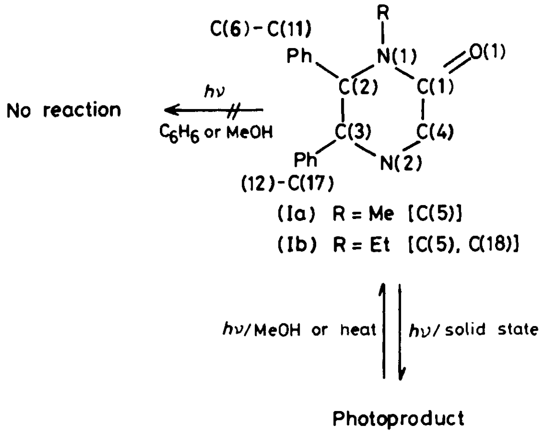
1-Methyl-5,6-diphenylpyrazin-2-one (Ia) crystallizes from ethanol in two crystal modifications; one is light stable and the other is light sensitive and undergoes photochemical [4 + 4] cyclodimerization in the solid state but not in a solution. The 1-ethyl derivative (Ib) is light stable. The crystal structures of the two modifications of (Ia) and (Ib), and that of the dimer, are described. The packing of the molecules in the unit cell plays a crucial role in the reactivity of the various compounds. The light-sensitive modification (Ia) is packed in parallel arrangement with short distances between the reacting centres. The light-stable modification has a different packing and the distances between possible reacting centres are too long to react (longer than 5.5 Å). The 1-ethyl derivative, although packed in a similar fashion to (Ia), is light stable. The distances between the possible reacting centres are longer than 4.2 Å, which is believed to be the distance limit for such a reaction to occur.

The course of certain types of solid-state reactions is determined by the geometry of the reactant lattice. In a long series of publications starting with a survey by Cohen and Schmidt,[1] who adopted Hertels phrase[2] ' topochemical ' factors, the dependence of the solid-state reaction on the relative geometry of the reactants in the crystal have been discussed. The postulate that such reactions occur with a minimum amount of atomic or molecular movements implies that the reactions are controlled by the relatively fixed distances and orientations, determined by the crystal structure, between potentially reactive centres. This postulate also suggests that an upper limit for such distances should exist for each type of reaction to occur. For intermolecular reactions, the geometry of the product (*e.g.* configuration) will be determined by the reactive orientation of molecules in the crystal lattice of the reactant molecules.

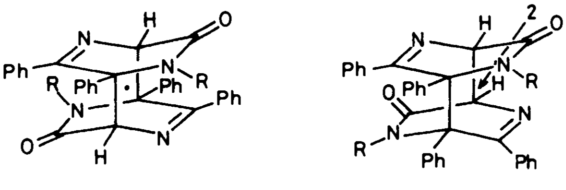
Photocyclodimerizations of [2 + 2] and [4 + 4] are perhaps the most thoroughly investigated solid-state photoreactions. Photochemical [4 + 4] cyclodimerization of aromatic compounds is a well established photoreaction; in particular, that which occurs in anthracenes[3] and in *p*-benzoquinone[4] and its various methyl derivatives. However, little attention has been given to such reactions that occur among the heteroaromatic compounds. Taylor and Kan,[5] Paquette and Slomp,[6] and de Mayo and Yip[7] have reported the results of photochemical [4 + 4] cyclodimerization of 2-pyridones and 2-pyrones in solution; a similar reaction of 4,6-diphenyl-2-pyrone in solution and in the solid state was reported by Rieke and Copenhafer.[8] The photoproduct obtained from the various compounds was assigned the *anti-trans* configuration. However, in a recent publication[9] it was shown that the [4 + 4] cycloaddition products formed on photodimerization of *N*-alkyl-2-pyridones are solvent dependent.

1-Methyl- (Ia) and 1-ethyl- (Ib) 5,6-diphenylpyrazin-2-one were inert to photolysis in benzene or methanol solution; however, it was reported[10] that irradiation of (Ia) in the solid state gave the [4 + 4] *anti-trans* dimer (Scheme). The structure was proposed on the basis of spectral data.

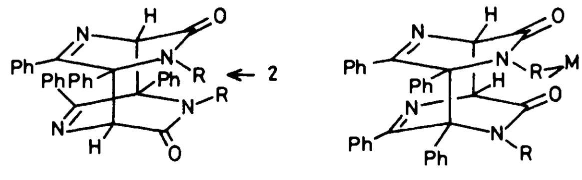
These observations suggest that the ability of the molecules to react is highly dependent upon the mutual orientation and the close proximity of possible reacting centres. It seems that those pre-reacting conditions are provided by the crystal lattice and are not achieved in the solution.



Scheme.



anti-trans *anti-cis*



syn-trans *syn-cis*

Figure 1. Four possible isomers of the photoproduct of the 1-methyl derivative (Ia)

The photoproduct of the 1-methyl derivative (Ia) may, in principle, adopt one of the four possible isomers shown in Figure 1. It is expected that the packing arrangement of molecules in the crystal of the light-sensitive modification will dictate the course of reaction, which in turn will lead to one of the four possible dimers.

Crystal structure elucidation will enable the correlation

Table 1. Atomic co-ordinates of (Ic) (× 10^4) for non-hydrogen atoms, (× 10^3) for hydrogens. U_{eq} ($Å^2 \times 10^3$) = $\frac{1}{3}$ trace $\tilde{U}$

Atom	x	y	z	U_{eq}
O(1)	10 968(2)	608(3)	2 297(3)	73(2)
N(1)	9 740(2)	400(3)	682(3)	45(1)
N(2)	10 466(2)	−2 043(3)	134(3)	50(1)
C(1)	10 578(3)	−42(3)	1 397(3)	50(2)
C(2)	9 260(2)	−349(3)	−272(3)	38(1)
C(3)	9 623(2)	−1 565(3)	−526(3)	43(1)
C(4)	10 912(3)	−1 310(4)	1 014(4)	50(2)
C(5)	9 343(3)	1 667(4)	1 058(5)	61(2)
C(6)	8 352(2)	220(3)	−957(3)	40(1)
C(7)	7 382(3)	−239(3)	−698(3)	47(2)
C(8)	6 542(3)	325(4)	−1 303(4)	56(2)
C(9)	6 670(3)	1 354(4)	−2 155(4)	58(2)
C(10)	7 630(3)	1 808(3)	−2 441(4)	56(2)
C(11)	8 471(3)	1 237(3)	−1 853(4)	49(2)
C(12)	9 133(2)	−2 494(3)	−1 472(3)	44(2)
C(13)	8 974(3)	−3 755(4)	−1 045(4)	55(2)
C(14)	8 533(3)	−4 645(4)	−1 899(5)	66(2)
C(15)	8 268(3)	−4 308(4)	−3 177(4)	63(2)
C(16)	8 423(3)	−3 076(4)	−3 616(4)	60(2)
C(17)	8 863(3)	−2 159(4)	−2 777(4)	51(2)
H(4)	1 155(3)	−160(3)	146(4)	
H(51)	962(4)	234(5)	29(4)	
H(52)	956(4)	183(5)	193(5)	
H(53)	866(5)	174(5)	99(6)	
H(7)	725(3)	−99(3)	−13(3)	
H(8)	588(4)	1(4)	−98(4)	
H(9)	609(3)	180(4)	−256(4)	
H(10)	775(3)	256(3)	−313(4)	
H(11)	906(3)	157(4)	−196(4)	
H(13)	911(3)	−392(4)	−14(4)	
H(14)	846(3)	−549(4)	−159(4)	
H(15)	795(3)	−497(4)	−379(4)	
H(16)	826(3)	−280(4)	−445(4)	
H(17)	900(2)	−126(4)	−307(3)	

Table 2. Atomic co-ordinates of (Ia) of the two independent molecules (A) and (B), (× 10^4) for non-hydrogen atoms, (× 10^3) for hydrogens. U_{eq} ($Å^2 \times 10^3$) = $\frac{1}{3}$ trace $\tilde{U}$

Atom	x	y	z	U_{eq}
Molecule (A)				
O(1)	2 017(1)	4 861	−9(2)	58(1)
N(1)	1 379(1)	4 955(6)	1 399(2)	37(1)
N(2)	2 735(1)	4 756(6)	3 189(2)	41(1)
C(1)	2 031(2)	4 883(7)	1 057(2)	42(2)
C(2)	1 400(2)	4 934(7)	2 609(3)	34(2)
C(3)	2 070(2)	4 789(7)	3 477(3)	39(2)
C(4)	2 699(2)	4 832(7)	2 060(3)	43(2)
C(5)	673(2)	4 914(11)	421(4)	50(2)
C(6)	677(2)	5 075(7)	2 903(3)	38(2)
C(7)	283(2)	6 879(8)	2 716(4)	50(2)
C(8)	−369(2)	7 047(10)	3 057(4)	60(3)
C(9)	−614(3)	5 401(10)	3 574(4)	73(4)
C(10)	−231(2)	3 612(10)	3 742(4)	70(3)
C(11)	416(2)	3 434(8)	3 492(4)	56(2)
C(12)	2 155(2)	4 603(7)	4 797(3)	37(2)
C(13)	1 888(2)	6 051(9)	5 430(4)	57(2)
C(14)	1 994(3)	5 853(10)	6 656(4)	70(3)
C(15)	2 345(2)	4 148(8)	7 266(4)	61(2)
C(16)	2 611(2)	2 700(8)	6 647(4)	51(2)
C(17)	2 524(2)	2 922(7)	5 420(3)	47(2)
H(4)	316(2)	470(6)	184(2)	
H(51)	27(2)	429(6)	62(3)	
H(52)	76(3)	410(9)	−23(5)	
H(53)	59(3)	619(10)	5(5)	
H(7)	45(2)	810(7)	245(3)	
H(8)	−61(2)	832(7)	291(3)	
H(9)	−102(2)	554(7)	381(3)	
H(10)	−40(4)	249(14)	420(6)	
H(11)	69(2)	210(7)	358(4)	
H(13)	166(3)	729(9)	499(4)	
H(14)	179(2)	674(8)	703(4)	
H(15)	243(2)	391(5)	814(3)	
H(16)	288(2)	145(8)	702(4)	
H(17)	274(2)	178(7)	492(4)	
Molecule (B)				
O(1)	1 079(1)	−137(6)	1 040(2)	59(1)
N(1)	2 214(1)	−197(6)	662(2)	40(1)
N(2)	2 901(2)	−53(6)	3 118(2)	45(2)
C(1)	1 767(2)	−162(7)	1 427(3)	42(2)
C(2)	2 988(2)	−179(7)	1 101(3)	37(2)
C(3)	3 316(2)	−69(7)	2 317(3)	36(2)
C(4)	2 180(2)	−145(8)	2 690(3)	48(2)
C(5)	1 815(2)	−205(10)	−640(3)	53(2)
C(6)	3 426(2)	−285(7)	209(3)	39(2)
C(7)	3 419(2)	−2 036(8)	−450(4)	50(2)
C(8)	3 856(3)	−2 135(9)	−1 226(4)	61(3)
C(9)	4 286(2)	−504(9)	−1 352(4)	65(3)
C(10)	4 287(3)	1 216(9)	−707(4)	61(3)
C(11)	3 853(2)	1 372(7)	72(4)	51(2)
C(12)	4 144(2)	149(6)	2 884(3)	37(2)
C(13)	4 646(2)	−1 276(8)	2 716(4)	54(2)
C(14)	5 403(2)	−1 022(9)	3 273(4)	63(3)
C(15)	5 658(2)	641(8)	3 987(4)	58(2)
C(16)	5 168(2)	2 078(8)	4 160(4)	54(2)
C(17)	4 403(2)	1 811(8)	3 618(3)	50(2)
H(4)	187(2)	−25(7)	330(3)	
H(51)	181(4)	146(14)	−95(7)	
H(52)	137(2)	56(7)	−74(3)	
H(53)	209(3)	−56(9)	−115(5)	
H(7)	315(2)	−320(6)	−32(3)	
H(8)	386(2)	−325(6)	−165(3)	
H(9)	457(2)	−75(6)	−191(3)	
H(10)	461(3)	242(10)	−77(4)	
H(11)	388(2)	253(8)	60(4)	
H(13)	447(2)	−259(7)	225(3)	
H(14)	575(3)	−200(9)	314(4)	
H(15)	618(2)	72(7)	438(3)	
H(16)	535(2)	337(9)	466(4)	
H(17)	406(2)	297(8)	372(3)	

between the packing of molecules in the three monomeric structures with the reactivity upon irradiation to be determined. Also, it will provide a test for the validity of some topochemical rules (which were stated for the [4 + 4] cyclodimerization of aromatic compounds) for heteroaromatic compounds.

Results

Crystal Structures of (Ia), (Ib), *and* (II).—Atomic positions for the light-stable modification of (Ia) [which will be referred to as (Ic)], the light-sensitive modification of (Ia), (Ib), and the dimer (II) are given in Tables 1, 2, 3, and 4, respectively. The bond lengths and angles for (Ia) and (Ic) are given in Tables 5 and 6, and for (Ib) and (II) are in Tables 7, 8, 9, and 10, respectively. The packing of molecules in the unit cell is shown stereoscopically in Figures 2, 3, 4, and 5.

The molecules in (Ic) (Figure 2) are not packed with their central planar portion in a parallel fashion, which is essential for the [4 + 4] cyclophotodimerization, the distances between possible reacting centres (marked in the drawing by the filled in circles) are too long to react (longer than 5.5 Å) and therefore it is not surprising that the modification is light stable.

The molecular packing in (Ia) and (Ib) is very similar

Table 3. Atomic co-ordinates of (Ib) of the two independent molecules (A) and (B), ($\times 10^4$) for non-hydrogen atoms, ($\times 10^3$) for hydrogens. U_{eq} ($Å^2 \times 10^3$) = $\frac{1}{3}$ trace $\tilde{U}$

Atom	x	y	z	U_{eq}
Molecule (A)				
O(1)	3 059(2)	1 812(2)	20(3)	74(1)
N(1)	2 258(2)	−44(2)	239(3)	44(1)
N(2)	3 863(2)	−938(2)	221(3)	53(1)
C(1)	3 057(2)	732(2)	129(3)	53(2)
C(2)	2 254(2)	−1 249(2)	383(3)	40(1)
C(3)	3 058(2)	−1 684(2)	372(3)	44(1)
C(4)	3 852(2)	181(3)	130(4)	56(2)
C(5)	1 410(2)	496(3)	94(4)	57(2)
C(6)	1 370(2)	−2 014(2)	542(3)	43(1)
C(7)	951(2)	−2 069(3)	1 899(4)	60(2)
C(8)	134(3)	−2 785(4)	2 056(6)	82(2)
C(9)	−271(3)	−3 460(4)	887(6)	81(2)
C(10)	140(3)	−3 435(3)	−450(5)	71(2)
C(11)	961(2)	−2 716(3)	−652(4)	53(2)
C(12)	3 142(2)	−2 961(2)	465(3)	45(1)
C(13)	2 699(2)	−3 773(3)	1 459(4)	56(2)
C(14)	2 823(2)	−4 939(3)	1 512(5)	66(2)
C(15)	3 379(3)	−5 324(3)	536(4)	66(2)
C(16)	3 838(3)	−4 524(3)	−438(4)	66(2)
C(17)	3 728(2)	−3 353(3)	−485(4)	54(2)
C(18)	1 244(3)	1 011(4)	1 574(5)	81(3)
H(4)	439(2)	71(3)	2(4)	
H(51)	148(2)	114(2)	−74(3)	
H(52)	91(2)	−15(3)	−22(3)	
H(7)	125(2)	−162(2)	273(4)	
H(8)	−9(3)	−275(3)	295(4)	
H(9)	−86(3)	−404(4)	101(6)	
H(10)	−9(3)	−392(3)	−132(5)	
H(11)	126(2)	−266(2)	−157(4)	
H(13)	236(2)	−349(2)	215(3)	
H(14)	248(2)	−552(3)	223(4)	
H(15)	348(2)	−612(3)	49(4)	
H(16)	426(2)	−479(3)	−109(4)	
H(17)	402(2)	−276(2)	−124(3)	
H(181)	173(3)	167(4)	183(5)	
H(182)	68(3)	139(4)	138(5)	
H(183)	108(3)	37(4)	234(6)	
Molecule (B)				
O(1)	1 960(2)	−1 697(2)	6 155(3)	81(1)
N(1)	2 734(2)	172(2)	5 936(3)	47(1)
N(2)	1 104(2)	1 025(2)	5 737(3)	56(1)
C(1)	1 943(2)	−627(3)	6 020(3)	55(2)
C(2)	2 715(2)	1 378(2)	5 754(3)	43(1)
C(3)	1 903(2)	1 792(2)	5 685(3)	44(2)
C(4)	1 133(2)	−95(3)	5 892(4)	59(2)
C(5)	3 590(2)	−337(3)	5 960(4)	63(2)
C(6)	3 594(2)	2 157(2)	5 525(3)	42(1)
C(7)	4 193(2)	2 553(3)	6 747(4)	53(2)
C(8)	4 999(2)	3 269(3)	6 483(5)	67(2)
C(9)	5 210(2)	3 575(3)	5 016(5)	72(2)
C(10)	4 616(3)	3 192(3)	3 801(5)	73(2)
C(11)	3 806(2)	2 489(3)	4 048(4)	55(2)
C(12)	1 800(2)	3 053(2)	5 541(3)	46(2)
C(13)	2 290(2)	3 889(3)	6 492(4)	65(2)
C(14)	2 146(3)	5 049(3)	6 360(5)	77(2)
C(15)	1 515(3)	5 402(3)	5 294(5)	74(2)
C(16)	1 017(3)	4 581(3)	4 338(4)	71(2)
C(17)	1 156(2)	3 427(3)	4 471(4)	58(2)
C(18)	3 734(4)	−727(5)	4 389(6)	92(3)
H(4)	60(2)	−63(3)	590(4)	
H(51)	348(2)	−109(3)	662(3)	
H(52)	411(2)	26(3)	647(4)	
H(7)	402(2)	231(2)	776(4)	
H(8)	540(3)	350(3)	735(5)	
H(9)	579(3)	409(3)	489(4)	
H(10)	475(2)	332(3)	270(4)	
H(11)	338(2)	221(3)	326(4)	
H(13)	269(2)	365(3)	732(4)	
H(14)	249(2)	566(3)	701(4)	
H(15)	142(2)	618(3)	518(4)	
H(16)	61(2)	486(3)	367(4)	
H(17)	81(2)	291(2)	380(3)	
H(181)	378(3)	−5(4)	359(6)	
H(182)	320(3)	−129(4)	407(5)	
H(183)	427(3)	−114(4)	445(5)	

Table 4. Atomic co-ordinates of (II) ($\times 10^4$) for non-hydrogen atoms, calculated positions ($\times 10^3$) for hydrogen atoms. U_{eq} ($Å^2 \times 10^3$) = $\frac{1}{3}$ trace $\tilde{U}$

Atom	x	y	z	U_{eq}
O(11)	3 776(3)	365(3)	2 709(3)	102(5)
N(11)	3 634(3)	−243(3)	2 013(3)	63(4)
N(21)	2 506(3)	−410(3)	2 391(3)	57(4)
C(11)	3 447(4)	109(4)	2 411(4)	72(6)
C(21)	3 198(3)	−506(3)	1 643(3)	56(5)
C(31)	2 681(4)	−708(4)	2 000(3)	55(5)
C(41)	2 792(4)	160(4)	2 459(3)	60(5)
C(51)	4 259(4)	−244(4)	1 883(5)	92(7)
C(61)	3 476(3)	−1 034(4)	1 381(4)	58(5)
C(71)	3 666(4)	−1 482(4)	1 713(4)	73(6)
C(81)	3 910(4)	−1 993(4)	1 518(5)	86(7)
C(91)	3 966(5)	−2 052(5)	966(6)	94(8)
C(101)	3 790(5)	−1 601(5)	639(4)	98(8)
C(111)	3 539(4)	−1 097(4)	844(4)	75(6)
C(121)	2 366(4)	−1 259(4)	1 877(4)	65(5)
C(131)	2 183(4)	−1 386(4)	1 371(4)	87(7)
C(141)	1 871(6)	−1 899(6)	1 273(6)	124(11)
C(151)	1 757(6)	−2 275(6)	1 683(9)	143(14)
C(161)	1 927(7)	−2 149(5)	2 196(7)	127(11)
C(171)	2 244(5)	−1 637(4)	2 291(4)	92(7)
O(12)	3 678(3)	718(3)	1 082(3)	102(5)
N(12)	3 012(3)	886(3)	1 740(3)	68(4)
N(22)	2 329(3)	28(3)	1 265(3)	58(4)
C(12)	3 249(4)	564(4)	1 351(4)	74(6)
C(22)	2 535(4)	626(3)	2 056(3)	56(5)
C(32)	2 126(4)	310(4)	1 656(3)	58(5)
C(42)	2 967(4)	−19(4)	1 242(3)	60(5)
C(52)	3 312(5)	1 406(5)	1 922(5)	117(9)
C(62)	2 191(4)	1 123(4)	2 319(4)	67(6)
C(72)	1 973(6)	1 551(5)	2 001(5)	127(10)
C(82)	1 653(8)	1 995(6)	2 221(6)	155(14)
C(92)	1 523(6)	2 012(5)	2 736(6)	114(10)
C(102)	1 710(6)	1 569(5)	3 046(5)	122(10)
C(112)	2 043(5)	1 131(4)	2 836(4)	95(7)
C(122)	1 481(4)	312(4)	1 730(4)	73(6)
C(132)	1 136(6)	503(8)	1 334(5)	170(15)
C(142)	517(7)	449(9)	1 408(8)	220(22)
C(152)	290(6)	233(8)	1 862(8)	148(14)
C(162)	635(6)	44(6)	2 224(7)	126(11)
C(172)	1 228(4)	85(5)	2 170(5)	96(8)
H(41)	273	30	281	
H(511)	444	15	203	
H(521)	437	−22	151	
H(531)	440	−58	192	
H(71)	362	−143	213	
H(81)	405	−234	178	
H(91)	415	−245	80	
H(101)	384	−164	22	
H(111)	340	−76	58	
H(131)	228	−109	105	
H(141)	173	−200	88	
H(151)	153	−268	161	
H(161)	182	−244	251	
H(171)	239	−154	268	
H(42)	303	−11	83	
H(512)	371	143	192	

Table 4 (*continued*)

Atom	*x*	*y*	*z*
H(522)	322	143	236
H(532)	319	177	169
H(72)	206	154	158
H(82)	149	234	197
H(92)	127	237	290
H(102)	160	156	346
H(112)	219	78	309
H(132)	132	69	98
H(142)	22	57	109
H(152)	−18	23	192
H(162)	45	−16	257
H(172)	150	−7	249

Table 5. Bond lengths (Å) in (Ia) molecules (A) and (B) and in (Ic). (C–H bond lengths lie in the range 0.86—1.15 Å)

Bond	(Ia) (A)	(Ia) (B)	(Ic)
O(1)–C(1)	1.228(4)	1.235(3)	1.233(4)
N(1)–C(1)	1.393(4)	1.389(4)	1.385(4)
N(1)–C(2)	1.391(4)	1.391(3)	1.378(3)
N(1)–C(5)	1.467(4)	1.472(4)	1.462(4)
N(2)–C(3)	1.384(4)	1.376(4)	1.376(3)
N(2)–C(4)	1.291(4)	1.297(4)	1.299(4)
C(1)–C(4)	1.437(4)	1.440(4)	1.437(4)
C(2)–C(3)	1.361(3)	1.362(4)	1.372(4)
C(2)–C(6)	1.497(4)	1.500(5)	1.493(4)
C(3)–C(12)	1.496(4)	1.505(4)	1.493(4)
C(6)–C(7)	1.381(6)	1.380(6)	1.379(4)
C(6)–C(11)	1.382(6)	1.390(6)	1.391(4)
C(7)–C(8)	1.398(6)	1.385(7)	1.383(5)
C(8)–C(9)	1.380(8)	1.377(7)	1.375(5)
C(9)–C(10)	1.364(8)	1.356(8)	1.371(5)
C(10)–C(11)	1.388(6)	1.386(7)	1.381(5)
C(12)–C(13)	1.383(6)	1.384(6)	1.391(5)
C(12)–C(17)	1.390(5)	1.383(5)	1.391(4)
C(13)–C(14)	1.381(6)	1.387(5)	1.382(6)
C(14)–C(15)	1.385(7)	1.370(7)	1.365(6)
C(15)–C(16)	1.373(7)	1.374(7)	1.365(6)
C(16)–C(17)	1.390(5)	1.399(5)	1.392(5)

(Figures 3 and 4). The molecules arranged in parallel stacks run along the shortest axis [6.584 Å in (Ia), 8.754 Å in (Ib)]. The stacks are composed of two crystallographically independent molecules with their central portions parallel to each other; the angles between the pyrazinone rings are 4.6 and 3.9°, respectively. However, while the independent molecules are related by a pseudo-two-fold axis in (Ia), they are related by a pseudo-inversion centre in (Ib).

The packing diagram for the molecules of (II) in the unit cell is shown in Figure 5. Within the channels formed along the *c* axis, solvent molecules (ethyl acetate) are occluded in a disordered fashion and have not been resolved. The molecular structure of the photodimer (II) (shown in Figure 6) is found to be the *syn-trans* isomer and not the *anti-trans* as proposed in the literature.[10] The structure obtained is in agreement with that expected when taking the packing of the reactant molecules (Ia) into account.

Bond lengths and angles for the five monomeric molecules are in good agreement. The phenyl rings are inclined to the pyrazinone moiety by angles ranging from 41.9 to 82.7°, depending on the variations in the molecular packing within the different structures.

Table 6. Bond angles (°) in (Ia) molecules (A) and (B) and in (Ic)

Bond	(Ia) (A)	(Ia) (B)	(Ic)
C(1)–N(1)–C(2)	121.2(3)	121.9(3)	121.9(2)
C(1)–N(1)–C(5)	116.6(2)	115.7(3)	116.5(2)
C(2)–N(1)–C(5)	122.0(2)	122.4(2)	121.4(2)
C(3)–N(2)–C(4)	117.6(3)	118.3(3)	118.0(2)
O(1)–C(1)–N(1)	121.8(3)	122.2(3)	121.4(3)
O(1)–C(1)–C(4)	124.5(3)	124.1(3)	124.6(3)
N(1)–C(1)–C(4)	113.7(2)	113.8(3)	114.0(2)
N(1)–C(2)–C(3)	119.4(2)	118.8(2)	119.2(2)
N(1)–C(2)–C(6)	118.0(3)	118.2(3)	117.1(2)
C(3)–C(2)–C(6)	122.5(2)	122.9(3)	123.7(2)
N(2)–C(3)–C(2)	121.7(2)	121.7(3)	121.4(2)
N(2)–C(3)–C(12)	114.4(3)	114.9(2)	114.4(2)
C(2)–C(3)–C(12)	123.9(2)	123.3(2)	124.2(2)
N(2)–C(4)–C(1)	126.2(2)	125.3(2)	125.4(3)
C(2)–C(6)–C(7)	119.8(3)	120.1(3)	120.7(2)
C(2)–C(6)–C(11)	120.2(3)	119.6(3)	120.3(2)
C(7)–C(6)–C(11)	119.9(3)	120.3(3)	119.0(2)
C(6)–C(7)–C(8)	119.8(4)	119.1(4)	120.2(3)
C(7)–C(8)–C(9)	119.4(5)	120.7(4)	120.0(3)
C(8)–C(9)–C(10)	120.8(4)	119.9(3)	120.5(3)
C(9)–C(10)–C(11)	120.0(5)	121.0(4)	119.6(3)
C(6)–C(11)–C(10)	120.0(4)	119.0(4)	120.6(3)
C(3)–C(12)–C(13)	122.7(4)	122.2(3)	118.6(3)
C(3)–C(12)–C(17)	118.8(3)	118.3(3)	122.5(2)
C(13)–C(12)–C(17)	118.5(3)	119.5(3)	118.8(3)
C(12)–C(13)–C(14)	121.0(5)	120.0(4)	120.2(3)
C(13)–C(14)–C(15)	120.3(5)	120.3(4)	120.6(4)
C(14)–C(15)–C(16)	119.2(4)	120.6(4)	120.0(4)
C(15)–C(16)–C(17)	120.7(4)	119.3(4)	120.6(3)
C(12)–C(17)–C(16)	120.3(3)	120.2(4)	119.7(3)

Table 7. Bond lengths (Å) in (Ib) molecules (A) and (B). (C–H bond lengths lie in the range 0.88—1.04 Å)

Bond	(A)	(B)
O(1)–C(1)	1.240(3)	1.234(3)
N(1)–C(1)	1.389(3)	1.391(3)
N(1)–C(2)	1.385(3)	1.393(3)
N(1)–C(5)	1.489(4)	1.488(4)
N(2)–C(3)	1.382(3)	1.378(3)
N(2)–C(4)	1.289(3)	1.296(4)
C(1)–C(4)	1.432(4)	1.434(4)
C(2)–C(3)	1.374(3)	1.369(3)
C(2)–C(6)	1.490(3)	1.499(3)
C(3)–C(12)	1.492(3)	1.481(3)
C(5)–C(18)	1.507(5)	1.511(6)
C(6)–C(7)	1.389(4)	1.379(3)
C(6)–C(11)	1.390(4)	1.381(4)
C(7)–C(8)	1.380(4)	1.385(4)
C(8)–C(9)	1.357(6)	1.368(6)
C(9)–C(10)	1.370(7)	1.367(5)
C(10)–C(11)	1.394(4)	1.380(4)
C(12)–C(13)	1.381(4)	1.381(4)
C(12)–C(17)	1.400(4)	1.383(4)
C(13)–C(14)	1.380(4)	1.381(5)
C(14)–C(15)	1.379(5)	1.358(5)
C(15)–C(16)	1.373(4)	1.377(5)
C(16)–C(17)	1.378(4)	1.372(5)

Discussion

The topochemical rules state that the stereochemistry of the dimer ($\bar{1}$ or m) is determined by the contact geometry [antiparallel ($\bar{1}$) or parallel (m)] of the nearest-neighbouring double bonds, provided that the centre-to-centre distance, *d*, of these double bonds is of the order of 4 Å (experimentally observed limits 4.2—3.5 Å).[11] It was also concluded that the exact parallel alignment, within a regular crystal lattice, of double bonds is an essential prerequisite for cyclodimerization.

In both 1-methyl (Ia) and 1-ethyl (Ib) derivatives, the molecules within a stack form two types of molecular pairs (con-

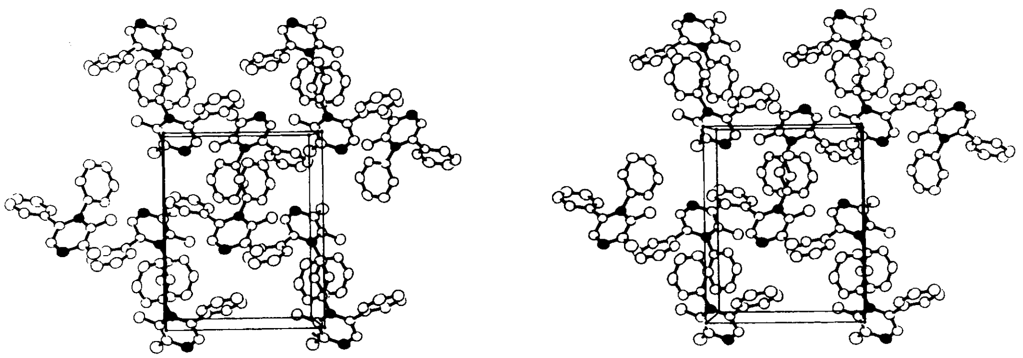


Figure 2. Packing of molecules in the unit cell of (Ic) (light-stable modification)

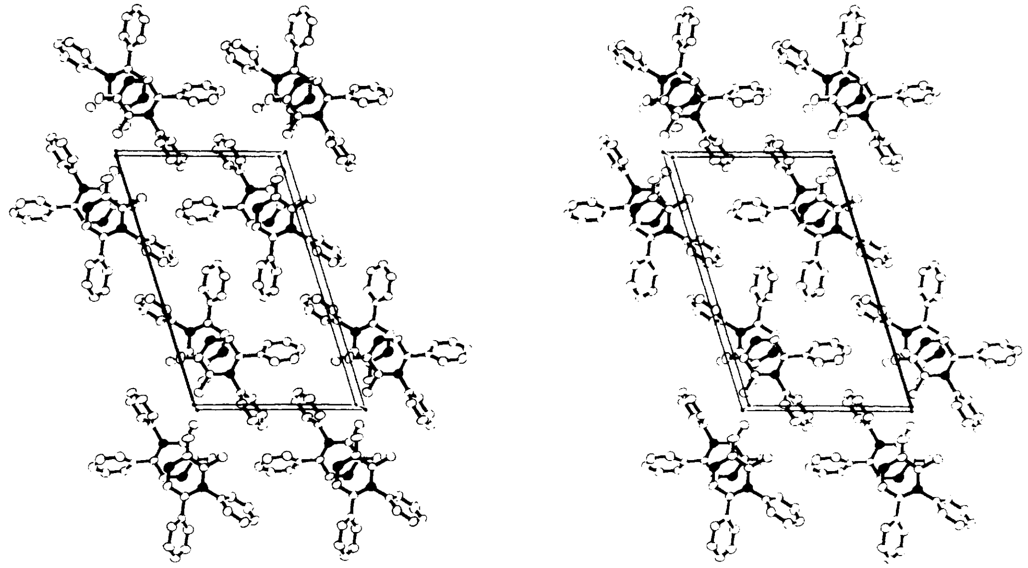


Figure 3. Packing of molecules in the unit cell of (Ia) (light-sensitive modification)

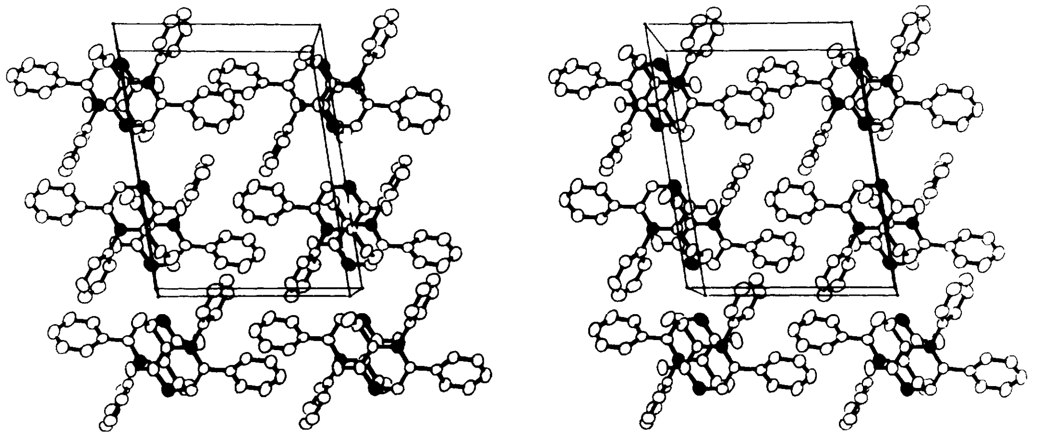


Figure 4. Packing of molecules in the unit cell of (Ib)

sisting of a reference molecule and the second independent molecular above or below it), which may lead to a photodimer. The different types of overlap diagrams of the two pairs in (Ia) are shown in Figure 7.

Although the topochemical rules state that parallel alignment of the double bonds is essential for [2 + 2] cyclodimerization, as the two reacting centres are within the same bond, it was found [12] that in some cases non-parallel double bonds may react. In some examples, such as in the photodimerization of coumarin, it was suggested that crystal faults may initiate the reaction; however, the increasing number of examples suggest that such assumptions should be reconsidered.

It is not surprising that in [4 + 4] cyclodimerization, where

Table 8. Bond angles (°) in (Ib) molecules (A) and (B)

Bond	(A)	(B)
C(1)–N(1)–C(2)	121.4(2)	121.5(2)
C(1)–N(1)–C(5)	115.9(2)	116.4(2)
C(2)–N(1)–C(5)	122.6(2)	122.1(2)
C(3)–N(2)–C(4)	118.7(2)	119.0(2)
O(1)–C(1)–N(1)	121.2(2)	121.3(2)
O(1)–C(1)–C(4)	124.1(3)	124.6(3)
N(1)–C(1)–C(4)	114.7(2)	114.0(2)
N(1)–C(2)–C(3)	119.1(2)	119.5(2)
N(1)–C(2)–C(6)	117.8(2)	117.3(2)
C(3)–C(2)–C(6)	123.1(2)	123.0(2)
N(2)–C(3)–C(2)	121.1(2)	120.7(2)
N(2)–C(3)–C(12)	114.5(2)	114.8(2)
C(2)–C(3)–C(12)	124.4(2)	124.5(2)
N(2)–C(4)–C(1)	125.1(3)	125.3(3)
N(1)–C(5)–C(18)	112.1(3)	111.4(3)
C(2)–C(6)–C(7)	120.8(2)	121.8(2)
C(2)–C(6)–C(11)	120.5(2)	118.9(2)
C(7)–C(6)–C(11)	118.7(2)	119.3(2)
C(6)–C(7)–C(8)	121.0(3)	119.9(3)
C(7)–C(8)–C(9)	120.4(4)	120.4(3)
C(8)–C(9)–C(10)	119.4(4)	119.9(3)
C(9)–C(10)–C(11)	121.7(4)	120.3(3)
C(6)–C(11)–C(10)	118.7(3)	120.2(3)
C(3)–C(12)–C(13)	124.0(2)	122.9(2)
C(3)–C(12)–C(17)	117.9(2)	119.9(2)
C(13)–C(12)–C(17)	118.1(2)	117.1(2)
C(12)–C(13)–C(14)	121.1(2)	121.1(3)
C(13)–C(14)–C(15)	120.3(3)	121.0(3)
C(14)–C(15)–C(16)	119.2(3)	118.9(3)
C(15)–C(16)–C(17)	120.9(3)	120.3(3)
C(12)–C(17)–C(16)	120.3(2)	121.7(3)

Table 9. Bond lengths (Å) in (II)

Bond	Length	Bond	Length
O(11)–C(11)	1.22(1)	C(161)–C(171)	1.40(1)
N(11)–C(11)	1.36(1)	O(12)–C(12)	1.25(1)
N(11)–C(21)	1.50(1)	N(12)–C(12)	1.34(1)
N(11)–C(51)	1.47(1)	N(12)–C(22)	1.48(1)
N(21)–C(31)	1.27(1)	N(12)–C(52)	1.45(1)
N(21)–C(41)	1.47(1)	N(22)–C(32)	1.27(1)
C(11)–C(41)	1.51(1)	N(22)–C(42)	1.47(1)
C(21)–C(31)	1.56(1)	C(12)–C(42)	1.51(1)
C(21)–C(61)	1.52(1)	C(22)–C(32)	1.56(1)
C(21)–C(42)	1.60(1)	C(22)–C(62)	1.54(1)
C(31)–C(121)	1.49(1)	C(32)–C(122)	1.49(1)
C(41)–C(22)	1.59(1)	C(62)–C(72)	1.36(1)
C(61)–C(71)	1.40(1)	C(62)–C(112)	1.35(1)
C(61)–C(111)	1.38(1)	C(72)–C(82)	1.37(1)
C(71)–C(81)	1.39(1)	C(82)–C(92)	1.34(2)
C(81)–C(91)	1.41(1)	C(92)–C(102)	1.35(1)
C(91)–C(101)	1.39(1)	C(102)–C(112)	1.37(1)
C(101)–C(111)	1.39(1)	C(122)–C(132)	1.35(1)
C(121)–C(131)	1.38(1)	C(122)–C(172)	1.36(1)
C(121)–C(171)	1.39(1)	C(132)–C(142)	1.44(2)
C(131)–C(141)	1.40(1)	C(142)–C(152)	1.36(2)
C(141)–C(151)	1.37(2)	C(152)–C(162)	1.29(2)
C(151)–C(161)	1.39(2)	C(162)–C(172)	1.37(1)

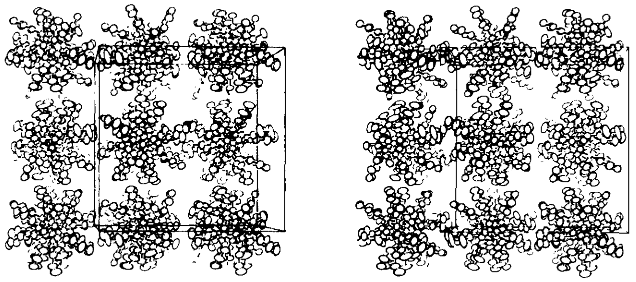


Figure 5. Packing of molecules in the unit cell of the photodimer (II)

the reaction does not occur between both ends of the double bonds, that this prerequisite condition is not fulfilled [the angles between C(2)=C(3) and N(2)=C(4) is 24°]. Nevertheless, the proximity of the reacting centres is important. These distances in (Ia) range from 3.456 to 3.640 Å, which are within the proposed limit.[11] Therefore the two pairs may, in principle, undergo photodimerization.

The two overlap diagrams observed in the crystal structure of (Ib) are shown in Figure 8. Substitution of the methyl by an ethyl group revealed dramatic changes regarding the centre-to-centre distances. In one of the pairs, the ethyl groups are pointing towards the centre of the neighbouring pyrazinone ring resulting in an increase in the reacting centre-to-centre distances to 5.538 and 5.656 Å (see Figure 8); in the other pair where the ethyl groups are pointing away from the neighbouring molecule the distances are shorter, 4.356 and 4.295 Å (see Figure 8). Although the distances are only slightly longer than the upper limit (4.2 Å), the crystalline compound is light stable under the same experimental conditions used for the photodimerization of the 1-methyl derivative.

An interesting feature emerges from the fact that the reactant molecules of the 1-methyl derivative are related within a pair by a pseudo-two-fold axis. It is also noted that this compound tends to crystallize in chiral crystals (spontaneous resolution) in either a $P2_1$ space group (the light-sensitive modification) or in a $P2_12_12_1$ space group (the light-stable modification).

The difference in handedness depends on the relative rotation of the phenyl substituents compared with the pyrazinone ring. It has long been recognized that the chemical transformation of a chiral crystalline specimen of one handedness containing a chiral educt into an optically active reaction product would constitute a novel asymmetric synthesis.[13] Extensive studies on solid-state photodimerization reactions of olefinic and related systems [11,14] have shown that the space symmetry which relates two reactant molecules in the starting material uniquely dictates the point symmetry of the dimeric photoproduct. It was shown [14] that in [2 + 2] cyclodimerization if the pre-reacting molecules are related by a two-fold axis parallel to the plane of interaction, an optically active product is anticipated. However, such solid-state photodimerizations are not common. If the monomers crystallize only in pairs a 100% optical yield may be anticipated; if each monomer has two potentially reactive neighbours then either a racemate or an optically active product is possible. The last statement is valid for the packing arrangement in (Ia). The two different pairs in (Ia) may react, hence if a single crystal of one handedness is irradiated, one out of three possible courses of reactions will take place. The three possible products are represented in Figure 9. If only the pairs (AB) react then the photodimer would be an optically active one; if on the other hand the pairs (BA) react, then the other enantiomeric photodimer would be obtained. If both pairs react, then a racemic mixture will be obtained.

The crystal structure of the photodimer (II) presented here shows that it crystallizes in racemic crystals; however, the irradiation was carried out on mixed-crystal specimens and therefore it is not significant in the possible mechanisms presented in Figure 9.

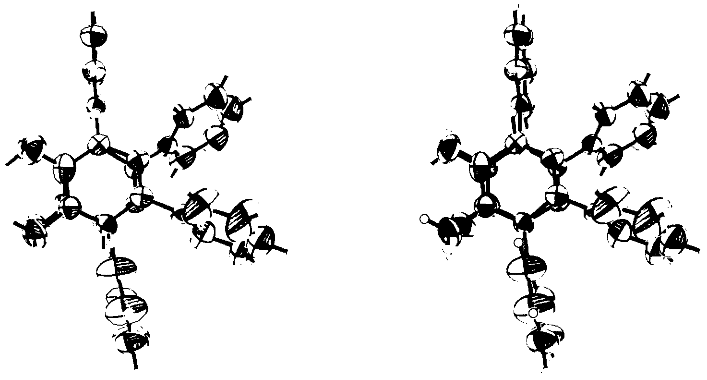


Figure 6. Stereoscopic view of the photodimer (II)

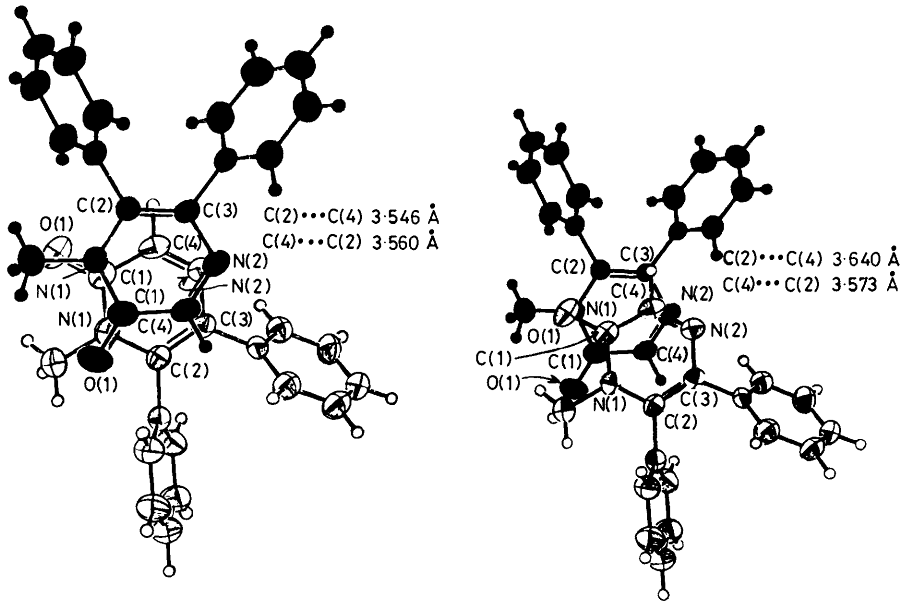


Figure 7. Two types of overlap diagrams of the two independent molecules in (Ia)

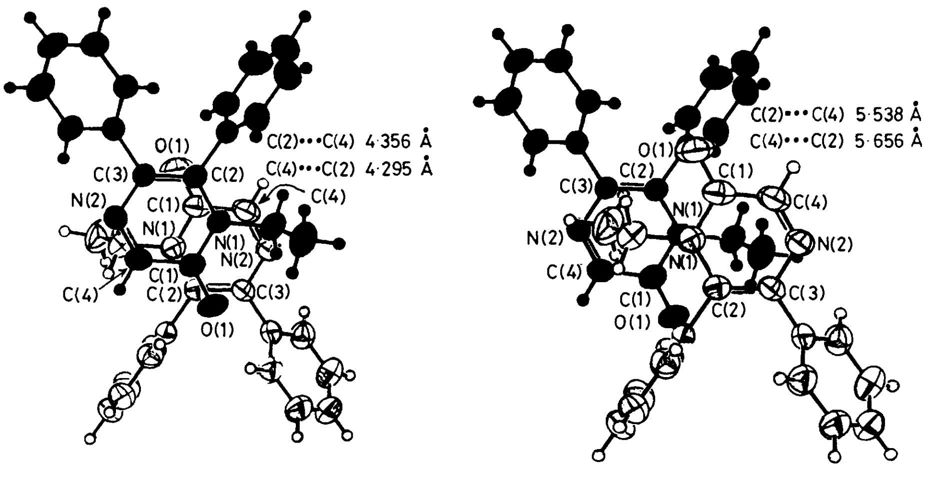


Figure 8. Two types of overlap diagrams of the two independent molecules in (Ib)

Table 10. Bond angles (°) in (II)

Bond	Angle	Bond	Angle
C(11)-N(11)-C(21)	119.5(6)	C(12)-N(12)-C(22)	118.4(6)
C(11)-N(11)-C(51)	118.2(7)	C(12)-N(12)-C(52)	119.4(8)
C(21)-N(11)-C(51)	120.8(7)	C(22)-N(12)-C(52)	120.5(7)
C(31)-N(21)-C(41)	115.3(6)	C(32)-N(22)-C(42)	115.7(6)
O(11)-C(11)-N(11)	123.5(8)	O(12)-C(12)-N(12)	124.4(8)
O(11)-C(11)-C(41)	121.9(8)	O(12)-C(12)-C(42)	119.1(8)
N(11)-C(11)-C(41)	114.7(7)	N(12)-C(12)-C(42)	116.5(8)
N(11)-C(21)-C(31)	105.3(6)	C(41)-C(22)-N(12)	110.1(6)
N(11)-C(21)-C(61)	108.2(6)	C(41)-C(22)-C(32)	109.1(6)
N(11)-C(21)-C(42)	109.8(6)	C(41)-C(22)-C(62)	114.2(6)
C(31)-C(21)-C(61)	109.6(6)	N(12)-C(22)-C(32)	106.2(6)
C(31)-C(21)-C(42)	109.0(6)	N(12)-C(22)-C(62)	108.4(6)
C(61)-C(21)-C(42)	114.6(6)	C(32)-C(22)-C(62)	108.5(6)
N(21)-C(31)-C(21)	122.2(7)	N(22)-C(32)-C(22)	121.6(7)
N(21)-C(31)-C(121)	117.8(7)	N(22)-C(32)-C(122)	117.6(7)
C(21)-C(31)-C(121)	119.9(7)	C(22)-C(32)-C(122)	120.8(7)
N(21)-C(41)-C(11)	111.5(6)	C(21)-C(42)-N(22)	110.8(6)
N(21)-C(41)-C(22)	110.9(6)	C(21)-C(42)-C(12)	111.0(6)
C(11)-C(41)-C(22)	111.5(6)	N(22)-C(42)-C(12)	110.8(6)
C(21)-C(61)-C(71)	116.9(7)	C(22)-C(62)-C(72)	117.7(8)
C(21)-C(61)-C(111)	124.0(7)	C(22)-C(62)-C(112)	123.9(7)
C(71)-C(61)-C(111)	119.0(7)	C(72)-C(62)-C(112)	118.1(9)
C(61)-C(71)-C(81)	122.1(9)	C(62)-C(72)-C(82)	119(1)
C(71)-C(81)-C(91)	118.1(9)	C(72)-C(82)-C(92)	122(1)
C(81)-C(91)-C(101)	120(1)	C(82)-C(92)-C(102)	118(1)
C(91)-C(101)-C(111)	121(1)	C(92)-C(102)-C(112)	120(1)
C(61)-C(111)-C(101)	119.9(8)	C(62)-C(112)-C(102)	121.7(9)
C(31)-C(121)-C(131)	121.5(8)	C(32)-C(122)-C(132)	119.1(9)
C(31)-C(121)-C(171)	117.9(8)	C(32)-C(122)-C(172)	121.7(8)
C(131)-C(121)-C(171)	120.6(8)	C(132)-C(122)-C(172)	118.9(9)
C(121)-C(131)-C(141)	120(1)	C(122)-C(132)-C(142)	117(1)
C(131)-C(141)-C(151)	119(1)	C(132)-C(142)-C(152)	121(1)
C(141)-C(151)-C(161)	121(1)	C(142)-C(152)-C(162)	120(1)
C(151)-C(161)-C(171)	119(1)	C(152)-C(162)-C(172)	121(1)
C(121)-C(171)-C(161)	120(1)	C(122)-C(172)-C(162)	122(1)

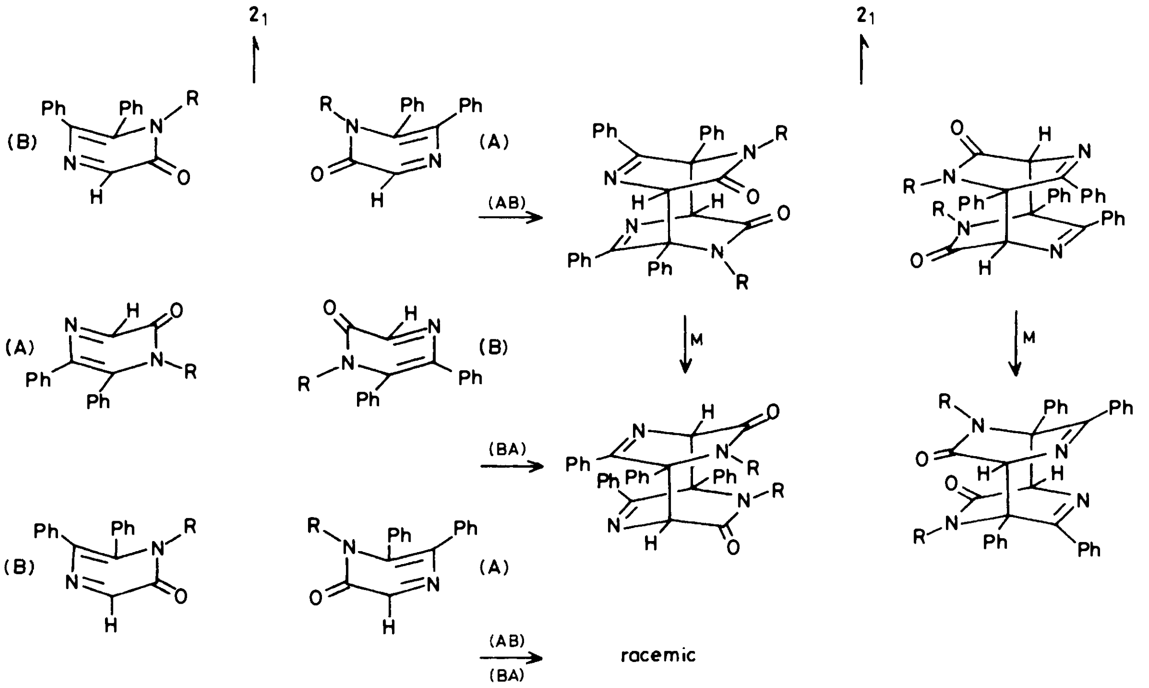


Figure 9. Possible mechanism for the photodimerization of a single crystal of (Ia)

This work is now continuing in the irradiation of a single crystal of the 1-methyl derivative, aimed at finding out the difference in the reactivity of the two different pairs of reactant molecules.

Conclusions

In view of the limited examples of cyclodimerization of heteroaromatic compounds in the solid state that were studied we cannot make conclusions regarding the similarities between the topochemical rules which are known to be valid for aromatic compounds and those obtained for heteroaromatic compounds. As the reacting centres in both systems are the same we may assume that such similarities do exist. In the present work it was shown that the upper limit of the distances between potentially reactive centres (4.2 Å) holds; however, the parallelism of the double bonds are not a prerequisite condition [1] for cyclodimerization in the solid state.

Experimental

Intensity data was measured with a PW1100 Philips four-circle computer-controlled diffractometer, with Mo-K_α radiation for (Ia), (Ib), and (Ic), and Cu-K_α for (II). The crystal structures were solved by MULTAN 80 [15] and refined by SHELX [16] using anisotropic vibrational parameters for O, N, and C atoms, and isotropic for H atoms. The scattering factors for O, N, and C were taken from Cromer and Mann [17] and for H from Stewart *et al.*[18] The list of observed and calculated structure factors is contained in Supplementary Publication No. SUP 23822 (70 pp.).*

1-*Methyl*-5,6-*diphenylpyrazin*-2-*one* (*light-sensitive modification*) (Ia).—$C_{17}H_{14}N_2O$, crystallizes from ethanol as yellowish prismatic plates,† monoclinic, $a = 18.765(9)$, $b = 6.584(4)$, $c = 11.585(6)$ Å, $\beta = 107.16(3)°$, space group $P2_1$, $Z = 4$, $R = 0.049$, $R_w = 0.047$ for 2 207 reflections $[F_0 > 1.5\sigma(F_0)]$. $[w = 1.1554/(\sigma^2(F) + 0.0003\,F^2)]$.

1-*Ethyl*-5,6-*diphenylpyrazin*-2-*one* (Ib).—$C_{18}H_{16}N_2O$, crystallizes from ethanol as yellowish prisms, triclinic, $a = 14.994(7)$, $b = 11.500(6)$, $c = 8.754(5)$ Å, $\alpha = 87.13(3)$, $\beta = 95.33(3)$, $\gamma = 98.81(3)°$, space group $P\bar{1}$, $Z = 4$, $R = 0.066$, $R_w = 0.075$ for 3 847 reflections $[F_0 > 1.5\sigma(F_0)]$. $[w = [1.4976/(\sigma^2(F) + 0.0024F^2)]$.

1-*Methyl*-5,6-*diphenylpyrazin*-2-*one* (*light-stable modification*) (Ic).—$C_{17}H_{14}N_2O$, crystallizes from ethanol as colourless prisms,† orthorhombic, $a = 13.082(6)$, $b = 10.374(5)$, $c = 9.963(5)$ Å, space group $P2_12_12_1$, $Z = 4$, $R = 0.051$, $R_w = 0.054$ for 1 372 reflections. $[w = 0.3949/(\sigma^2(F) + 0.0031F^2)]$.

Photodimer (II).—$C_{34}H_{28}N_4O_2$, crystallizes from ethyl acetate as colourless prisms, tetragonal, $a = b = 22.93(1)$, $c = 25.35(1)$ Å, space group $I4_1/a$, $Z = 16$. The compound crystallizes with solvent molecules. During the intensity measurements the crystal loses the solvent and becomes opaque. Although the structure of the dimer was solved with no difficulties the refinement procedure did not reveal an accurate structure; some of the hydrogen atoms appeared in the difference Fourier maps; however, the positions of some were calculated and not refined. Some atoms of the phenyl rings suffered from high thermal motions. Remaining electron densities appeared around a two-fold axis and were attributed to two disordered ethyl acetate molecules. However, introducing some of the remaining electron densities as atoms did not reveal meaningful chemical fragments. The refinement procedure was stopped at $R = 0.11$ using unit weight for 3 302 reflections $[F_0 > 5.0\sigma(F_0)]$. Although the crystal structure is not well refined, there is no doubt regarding the molecular structure of the dimer.

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* For details of the Supplementary Publications Scheme, see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

† Both isomers [(Ia) and (Ic)] crystallize from ethanol and the nature or the conditions by which one can control the crystallization of an individual isomer is not known.