

Studies on Flavin derivatives. The Crystal and Molecular Structure of 4a-Allyl-3,5,7,8,10-pentamethyl-4a,5-dihydroisoalloxazine

BY ROLF NORRESTAM

Institute of Inorganic and Physical Chemistry, University of Stockholm, S-104 05 Stockholm, Sweden

(Received 29 December 1971)

The crystal structure of 4a-allyl-3,5,7,8,10-pentamethyl-4a,5-dihydroisoalloxazine, $C_{18}H_{22}N_4O_2$, has been derived from three-dimensional X-ray diffractometer data. The unit cell is orthorhombic, space group $P2_12_12_1$, $Z=4$, with the dimensions $a=17.422$, $b=12.777$ and $c=7.564$ Å. The structure was determined by direct methods (variance-weighted Σ_2 formula). Full-matrix least-squares refinement of the structural parameters gave an unweighted linear R value of 0.035 for 1608 observed reflexions. The 4a-allyl-substitution gives bond angles around the carbon atom C(4a) of about 109.5° . The presence of this tetrahedral carbon atom causes a slight twist of the molecules along the alloxazine ring system. The intermolecular contacts suggest that the crystal structure is largely held together by conventional van der Waals forces.

Introduction

The flavoenzymes, which have an isoalloxazine moiety as a part of the prosthetic group, form a class of redox-active enzymes playing an important role in biological redox processes (see *e.g.* Ehrenberg & Hemmerich, 1968). The isoalloxazine group occurs in three different states of oxidation – the oxidized, the radical (mono-hydroisoalloxazine) and the fully reduced (dihydroisoalloxazine) states. The present structure determination of 4a-allyl-3,5,7,8,10-pentamethyl-4a,5-dihydroisoalloxazine (Fig. 1) is part of a series of structural investigations of flavin derivatives (*cf.* Kierkegaard *et al.*, 1971) undertaken at this Institute.

In previous papers we have shown that the isoalloxazine ring of neutral (non-protonated) derivatives is bent in fully reduced 1,5-dihydroisoalloxazines (see *e.g.* Norrestam, von Glehn, Hagman & Kierkegaard, 1969) and planar in oxidized isoalloxazines (Norrestam & Stensland, 1972). The present investigation will provide structural information about another group of fully reduced derivatives, the 4a,5-dihydroisoalloxazines.

A number of biochemical studies support the fact that irreversible flavin reduction, giving 4a,5-dihydro-compounds, does occur (see *e.g.* Gavron, 1963). The possible role of 4a-substituted flavins as intermediates in group transfer processes during the catalysis of flavin enzymes has been extensively studied (*cf.* Walker, Hemmerich & Massey, 1967 and Hemmerich, Ghisla, Hartman & Müller, 1971).

Experimental

A crystalline specimen of 4a-allyl-3,5,7,8,10-pentamethyl-4a,5-dihydroisoalloxazine was kindly supplied by Dr S. Ghisla (University of Konstanz, Germany).

The preparation of some other 4a,5-dihydroalloxazines is described by Jefcoate, Ghisla & Hemmerich (1971). The crystals were examined by X-ray photographic methods (Guinier, oscillation and Weissenberg techniques). The X-ray photographs indicated orthorhombic symmetry and the systematic extinctions among the reflexions were consistent with space group $P2_12_12_1$. The crystal finally selected had the dimensions $0.20 \times 0.30 \times 0.22$ mm, with the prismatic axis along [010], and was mounted on a goniometer along this axis. Precise unit cell parameters were obtained by least-squares refinement of manual single-crystal diffractometer measurements with Cu $K\alpha$ radiation ($\lambda = 1.54184$ Å).

Crystal data

Composition of asymmetric unit $C_{18}H_{22}N_4O_2$, (calculated molecular weight = 326.4); $a=17.422$ (5), $b=12.777$ (3), $c=7.564$ (5) Å, $V_0=1683.8$ Å³, $D_c=1.29$ g.cm⁻³, $Z=4$, $\mu(\text{Cu } K\alpha)=7.1$ cm⁻¹, space group = $P2_12_12_1$.

Three-dimensional X-ray intensity data were collected on a Siemens AED single-crystal diffractometer with graphite-monochromatized Cu K radiation, using a scintillation detector with pulse height discrimination. The 1789 independent reflexions within $\theta \leq 68^\circ$ were measured with the θ - 2θ scan technique (scan interval 1.6°) and the background intensity for each reflexion was calculated as the average of the intensities measured at each of the ends of the scan interval. To facilitate a judgement of the random counting errors of the data, a plot of the percentage of the collected data with $\sigma(I_{\text{net}})/I_{\text{net}} \leq \sigma_{\text{rel}}$ versus σ_{rel} was performed and is shown in Fig. 2. The calculation of the e.s.d.'s of the net intensities, $\sigma(I_{\text{net}})$, was based on conventional counter statistics. Only the 1613 independent reflexions (90%) for which $\sigma(I_{\text{net}})/I_{\text{net}} \leq 0.10$ were used in the subsequent calculations. The net

intensities were corrected for Lorentz, polarization and absorption effects (the transmission factors varied between 0.84 and 0.88.)

Structure determination and refinement

The crystal structure was solved by application of direct methods (see *e.g.* Karle & Karle, 1966) in which variance-weighted \sum_2 relations were used for estimation and refinement of phases. A detailed description of the phasing programs is given elsewhere (Norrestam, 1972).

Approximate overall temperature and scale factors were obtained from a usual Wilson plot using a local version of the program *FAME* (Dewar & Stone). The statistical averages and distribution of the derived normalized structure factors $|E|$ are given in Table 1. From the 205 highest $|E|$'s ($|E|$ greater than 1.5), the 914 best triple-phase relations having $|E(\mathbf{h})E(-\mathbf{k})E(\mathbf{k}-\mathbf{h})|$ greater than 12.0 (the variances of the relations used will then be below 0.6 rad², according to the table given by Germain, Main & Woolfson, 1970). Of the 205 reflexions used for generating triple relations, thirteen ($|E|$'s below 1.8) did not enter into any relations.

Table 1. *Statistical data for the normalized structure factors*

	Experi- mental	Theoretical centrosymmetric	Theoretical non-centrosymmetric
$\langle E \rangle$	0.80	0.798	0.886
$\langle E ^2 - 1 \rangle$	1.000	1.000	1.000
$\langle E ^2 \rangle$	0.94	0.968	0.736
$ E > 1$	29.0 %	32.0 %	37.0 %
$ E > 2$	3.9	5.0	1.8
$ E > 3$	1.0	0.30	0.01

Several \sum_1 relations indicated that the phases of the reflexions 022 and 14,0,0 were both 0.0 radians (estimated probabilities above 0.9). Analysis of the 914 triple relations showed that the reflexions 783 and 892 entered into several relations involving two reflexions whose phase sums were known from symmetry imposed phase restrictions to be $\pi/2$, modulus π . By assigning the value $\pi/2$ to these two reflexions, and the value $\pi/4$ to the reflexion 6,11,1, a proper set of origin and enantiomorph-defining reflexions was obtained.

To obtain phases of most of the 192 reflexions involved in the triple relations, two unknowns, 043 and 012, were included in the basis set. These two reflexions have restricted phases, so that four alternative possible solutions existed. The basis set used and the phases obtained by the phasing program, together with the phases calculated after completion of the structure determination, are given in Table 2.

For each of the four solutions, four different figures of merit were calculated, *viz.* the number of phases determined with e.s.d.'s below $\pi/4$, the number of triple relations having phase-sums between $-\pi/4$ and $\pi/4$, the r.m.s. deviation of the triple-phase sums from

Table 2. *Basis set used for solving the phase relations*

Indices	$ E $ value	Initial phase value	Refined phase value	Calculated phase value
7 8 3	3.86	$\pi/2$	1.64	1.76
6 11 1	3.39	$\pi/4$	1.26	0.44
8 9 2	3.29	$\pi/2$	1.99	2.17
0 4 3	4.39	π	π	π
0 1 2	3.04	$\pi/2$	$\pi/2$	$\pi/2$
0 2 2	3.19	0	0	0
14 0 0	2.59	0	0	0

zero and the sum $\sum |E_i| \cos \varphi_i$ (where φ_i is the phase for reflexion number i). The solution giving the most promising figures of merit was used to calculate an *E* map.

The fifteen highest peaks in this map made chemical sense and their positions together with isotropic temperature factors (initialized 3.0 Å²) and one overall scale-factor were refined by four cycles of full-matrix least-squares treatment, to yield an unweighted *R* value ($R = \sum |k|F_o| - |F_c| / \sum k|F_o|$) of 0.41 for all 1613 reflexions. At this stage all the atoms were treated as carbons. From a subsequent difference electron density map, three more atoms were located. From knowledge of

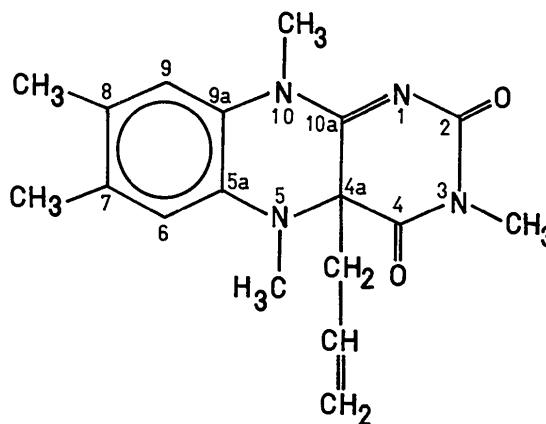


Fig. 1. Schematic drawing of 4a-allyl-3,5,7,8,10-pentamethyl-4a,5-dihydroisoalloxazine, with atoms within the rings numbered for reference in the text.

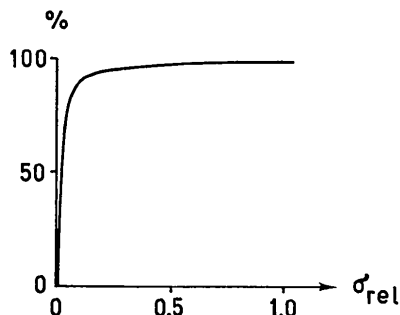


Fig. 2. Percentage of the collected data with $\sigma(I_{\text{net}})/I_{\text{net}} \leq \sigma_{\text{rel}}$ plotted versus σ_{rel} .

the schematic structural formula (*cf.* Fig. 1), it was possible to identify the 18 atoms and thus assign proper scattering factors to them in the calculation of difference electron densities, from which the remaining 6 non-hydrogen atoms were located. Four cycles of least-squares refinement of the 24 non-hydrogens with anisotropic temperature factors reduced the *R* value to 0.072. Reasonable positions for the 22 hydrogens were easily found from a subsequent difference electron density map. Refinement of the obtained structure model with anisotropic temperature factors for the non-hydrogen and isotropic ones for the hydrogen atoms gave a final *R* value of 0.041, for all 1613 reflexions. The finally obtained structure factors $k|F_o|$ and $|F_c|$ are listed in Table 3. Inspection of this list shows that at least the five strongest reflexions, all having fairly low $\sin \theta$ values, appear to suffer from extinction since their $|F_o|$ values are much smaller than their $|F_c|$ values. Upon omission of these five reflexions, the *R* value for the remaining 1608 reflexions becomes 0.035.

In all the refinements Hughes's (1941) weighting scheme with $|F_o|_{\min} = 1.5$ was used. The scattering factors used for carbon, nitrogen and oxygen were those given by Hanson, Herman, Lea & Skillman (1964), for

Table 3 (*cont.*)

13	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000	1001	1002	1003	1004	1005	1006	1007	1008	1009	1010	1011	1012	1013	1014	1015	1016	1017	1018	1019	1020	1021	1022	1023	1024	1025	1026	1027	1028	1029	1030	1031	1032	1033	1034	1035	1036	1037	1038	1039	1040	1041	1042	1043	1044	1045	1046	1047	1048	1049	1050	1051	1052	1053	1054	1055	1056	1057	1058	1059	1060	1061	1062	1063	1064	1065	1066	1067	1068	1069	1070	1071	1072	1073	1074	1075	1076	1077	1078	1079	1080	1081	1082	1083	1084	1085	1086	1087	1088	1089	1090	1091	1092	1093	1094	1095	1096	1097	1098	1099	1100	1101	1102	1103	1104	1105	1106	1107	1108	1109	1110	1111	1112	1113	1114	1115	1116	1117	1118	1119	1120	1121	1122	1123	1124	1125	1126	1127	1128	1129	1130	1131	1132	1133	1134	1135	1136	1137	1138	1139	1140	1141	1142	1143	1144	1145	1146	1147	1148	1149	1150	1151	1152	1153	1154	1155	1156	1157	1158	1159	1160	1161	1162	1163	1164	1165	1166	1167	1168	1169	1170	1171	1172	1173	1174	1175	1176	1177	1178	1179	1180	1181	1182	1183	1184	1185	1186	1187	1188	1189	1190	1191	1192	1193	1194	1195	1196	1197	1198	1199	1200	1201	1202	1203	1204	1205	1206	1207	1208	1209	1210	1211	1212	1213	1214	1215	1216	1217	1218	1219	1220	1221	1222	1223	1224	1225	1226	1227	1228	1229	1230	1231	1232	1233	1234	1235	1236	1237	1238	1239	1240	1241	1242	1243	1244	1245	1246	1247	1248	1249	1250	1251	1252	1253	1254	1255	1256	1257	1258	1259	1260	1261	1262	1263	1264	1265	1266	1267	1268	1269	1270	1271	1272	1273	1274	1275	1276	1277	1278	1279	1280	1281	1282	1283	1284	1285	1286	1287	1288	1289	1290	1291	1292	1293	1294
----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------

sion of the program *LALS* (Gantzel, Sparks & Trueblood).

The molecular conformation, together with the atomic labels used, is shown in Fig. 3. In Tables 4, 5 and 6, the positional and thermal parameters are given with their e.s.d.'s. Tables 7 and 8 show the intramolecular bond distances and angles uncorrected for thermal vibration.

After the completion of the structure determination, the phases obtained from the phasing program were compared with the phases calculated in the last least-squares cycle. The average deviation of all the 145 phases determined with e.s.d.'s below 45° was 14°. The average deviation of the phases for the 88 reflexions having phase values not restricted by space group symmetry, was 23°. This last deviation, 23°, is somewhat higher than those usually obtained (about 15–20°) for structures of similar complexity treated by the variance-weighted Σ_2 formula. A possible explanation (Hauptman, 1964) is the large overlap in Patterson space for crystal structures built up of roughly planar molecules consisting of hexagons and having fairly parallel molecular planes. However, the *E* map did not show any of the confusing spurious peaks to be expected, according to Bürgi & Dunitz (1971), for such structures.

A comparison between the phases obtained by the so called weighted Σ_2 formula (Karle & Karle, 1966), and by the variance-weighted Σ_2 formula used in the present study, showed that the average deviation of the phases not restricted by symmetry became 31 and 23° respectively. Thus, the more proper weighting used in

the latter case produces significantly improved phase-estimates.

Discussion

The crystal structure projected on (001) and (010) is shown in Fig. 4. The fairly planar molecules are oriented in such a way that their molecular planes are almost parallel and perpendicular to the *c* direction. Lack of proper hydrogen donors precludes conventional hydrogen-bond formation in the crystal struc-

Table 6. *Hydrogen fractional atomic coordinates and isotropic temperature factors*

The estimated standard deviations are given in parentheses

H(6)	0.380 (1)	0.210 (2)	0.736 (3)	3.2 (4) Å ²
H(9)	0.366 (1)	0.552 (2)	0.956 (3)	3.3 (4)
H(13a)	0.817 (3)	0.358 (4)	0.679 (10)	12.9 (18)
H(13b)	0.795 (3)	0.284 (5)	0.652 (9)	12.1 (20)
H(13c)	0.804 (4)	0.244 (5)	0.818 (9)	13.5 (17)
H(14a)	0.508 (1)	0.468 (2)	0.577 (3)	2.7 (4)
H(14b)	0.598 (1)	0.464 (2)	0.520 (3)	3.9 (5)
H(15a)	0.560 (2)	0.247 (3)	1.022 (5)	5.8 (7)
H(15b)	0.576 (2)	0.161 (2)	0.867 (4)	4.8 (6)
H(15c)	0.494 (2)	0.160 (2)	0.939 (4)	5.4 (7)
H(17a)	0.202 (2)	0.256 (2)	0.884 (5)	5.1 (7)
H(17b)	0.244 (2)	0.181 (3)	0.758 (5)	6.8 (8)
H(17c)	0.202 (2)	0.292 (3)	0.701 (6)	7.7 (10)
H(18a)	0.234 (2)	0.553 (3)	0.951 (6)	8.8 (10)
H(18b)	0.192 (2)	0.472 (3)	0.830 (5)	6.2 (8)
H(18c)	0.200 (2)	0.446 (3)	1.013 (6)	7.2 (9)
H(20a)	0.556 (2)	0.570 (3)	1.114 (5)	6.5 (8)
H(20b)	0.490 (2)	0.635 (4)	0.985 (7)	8.7 (10)
H(20c)	0.472 (2)	0.563 (3)	1.153 (6)	7.8 (9)
H(24)	0.565 (2)	0.304 (3)	0.357 (6)	8.6 (10)
H(34a)	0.425 (2)	0.392 (3)	0.380 (5)	6.8 (8)
H(34b)	0.445 (2)	0.300 (3)	0.235 (5)	6.4 (8)

Table 5. *Anisotropic thermal parameters for the nonhydrogen atoms*

The estimated standard deviations are given in parentheses. The temperature factor expression used is

$$\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$$

	$b_{11} \times 10^4$	$b_{22} \times 10^4$	$b_{33} \times 10^4$	$b_{12} \times 10^4$	$b_{13} \times 10^4$	$b_{23} \times 10^4$
N(1)	23 (1)	50 (1)	214 (4)	-14 (1)	-9 (2)	-43 (3)
C(2)	23 (1)	57 (1)	196 (4)	-12 (1)	-8 (3)	-5 (4)
N(3)	18 (1)	52 (1)	181 (3)	-2 (1)	4 (2)	18 (3)
C(4)	21 (1)	38 (1)	157 (3)	-4 (1)	13 (2)	20 (3)
C(4a)	19 (1)	34 (1)	137 (3)	-5 (1)	2 (2)	4 (3)
N(5)	20 (1)	32 (1)	142 (3)	-6 (1)	3 (2)	3 (2)
C(5a)	20 (1)	35 (1)	116 (3)	-2 (1)	5 (2)	2 (3)
C(6)	24 (1)	41 (1)	138 (3)	-11 (1)	3 (2)	-3 (3)
C(7)	21 (1)	57 (1)	127 (3)	-9 (1)	1 (2)	8 (3)
C(8)	22 (1)	61 (1)	144 (3)	7 (1)	7 (3)	10 (4)
C(9)	24 (1)	42 (1)	162 (3)	7 (1)	9 (2)	-10 (3)
C(9a)	21 (1)	37 (1)	127 (3)	-4 (1)	6 (2)	-2 (3)
N(10)	22 (1)	36 (1)	171 (3)	-3 (1)	1 (2)	-35 (3)
C(10a)	21 (1)	33 (1)	157 (3)	-7 (1)	-2 (2)	0 (3)
O(12)	23 (1)	95 (1)	341 (5)	-33 (1)	-20 (3)	-84 (5)
C(13)	20 (1)	75 (2)	253 (5)	7 (2)	18 (3)	12 (6)
O(14)	26 (1)	50 (1)	237 (3)	6 (1)	22 (2)	-53 (3)
C(14a)	24 (1)	40 (1)	156 (4)	-5 (1)	12 (2)	26 (3)
C(15)	26 (1)	47 (1)	201 (4)	10 (1)	11 (3)	56 (4)
C(17)	23 (1)	84 (2)	208 (5)	-18 (2)	4 (3)	-9 (5)
C(18)	24 (1)	87 (2)	264 (6)	16 (2)	12 (4)	-46 (6)
C(20)	32 (1)	48 (2)	215 (5)	-9 (2)	9 (3)	-75 (4)
C(24a)	32 (1)	57 (1)	146 (4)	12 (1)	11 (2)	6 (4)
C(34a)	38 (1)	74 (2)	179 (4)	-12 (2)	-20 (3)	12 (5)

ture. Most of the intermolecular distances (Table 9) are of the same order as van der Waals distances. The largest deviations from van der Waals contact distances occur between the keto oxygen atoms, O(12) and O(14), carrying negative atomic charges, and various other atoms, most of which probably have small positive atomic charges. Thus the crystal structure is probably held together largely by conventional van der Waals forces between molecules oriented in an electrostatically favourable way.

As seen from Table 10, the isalloxazine ring system is not strictly planar. The r.m.s. deviations of the atoms from the least-squares plane (labelled I in Table 10), through the atoms forming the ring system are as high as 0.19 Å. The largest deviations from the least squares plane occur for atoms C(4), C(4a) and N(5) (-0.23,

-0.46 and 0.25 Å respectively). This distortion of the planarity of the ring system is obviously due to the large C(sp³) character of the C(4a) atom. Thus, the average of the six bond angles (*cf.* Table 8) at C(4a) is

Table 8. *Intramolecular bond angles* (°)

Only bond angles involving non-hydrogen atoms are given. The estimated standard deviations are given in parentheses.

C(10a)—N(1)—C(2)	119.6 (2)
N(1)—C(2)—N(3)	120.2 (2)
N(1)—C(2)—O(12)	121.3 (2)
N(3)—C(2)—O(12)	118.4 (2)
C(2)—N(3)—C(4)	124.0 (2)
C(2)—N(3)—C(13)	117.7 (2)
C(4)—N(3)—C(13)	118.2 (2)
N(3)—C(4)—C(4a)	117.1 (2)
N(3)—C(4)—O(14)	122.2 (2)
C(4a)—C(4)—O(14)	120.6 (2)
C(4)—C(4a)—N(5)	109.4 (1)
C(4)—C(4a)—C(10a)	111.5 (2)
C(4)—C(4a)—C(14a)	107.2 (2)
N(5)—C(4a)—C(10a)	111.6 (2)
N(5)—C(4a)—C(14a)	111.2 (1)
C(10a)—C(4a)—C(14a)	105.8 (1)
C(4a)—N(5)—C(5a)	111.1 (1)
C(4a)—N(5)—C(15)	115.7 (1)
C(5a)—N(5)—C(15)	112.6 (2)
N(5)—C(5a)—C(6)	121.0 (2)
N(5)—C(5a)—C(9a)	120.6 (2)
C(6)—C(5a)—C(9a)	118.5 (2)
C(5a)—C(6)—C(7)	122.4 (2)
C(6)—C(7)—C(8)	118.7 (2)
C(6)—C(7)—C(17)	120.1 (2)
C(8)—C(7)—C(17)	121.2 (2)
C(7)—C(8)—C(9)	118.9 (2)
C(7)—C(8)—C(18)	121.5 (2)
C(9)—C(8)—C(18)	119.6 (2)
C(8)—C(9)—C(9a)	121.9 (2)
C(9)—C(9a)—N(10)	122.2 (2)
C(5a)—C(9a)—C(9)	119.6 (2)
C(5a)—C(9a)—N(10)	118.2 (2)
C(9a)—N(10)—C(10a)	121.3 (2)
C(9a)—N(10)—C(20)	118.8 (2)
C(10a)—N(10)—C(20)	119.8 (2)
N(10)—C(10a)—N(1)	119.5 (2)
C(4a)—C(10a)—N(1)	115.2 (2)
N(1)—C(10a)—C(4a)	125.2 (2)
C(4a)—C(14a)—C(24a)	114.8 (2)
C(14a)—C(24a)—C(34a)	124.2 (2)

Table 7. *Intramolecular bond distances in Å with estimated standard deviations in parentheses*

N(1)—C(2)	1.374 (3)
C(2)—N(3)	1.410 (2)
N(3)—C(4)	1.366 (2)
C(4)—C(4a)	1.526 (2)
C(4a)—N(5)	1.465 (2)
N(5)—C(5a)	1.421 (2)
C(5a)—C(6)	1.389 (3)
C(6)—C(7)	1.388 (3)
C(7)—C(8)	1.411 (3)
C(8)—C(9)	1.387 (3)
C(9)—C(9a)	1.387 (3)
C(9a)—N(10)	1.424 (2)
N(10)—C(10a)	1.347 (2)
C(10a)—N(1)	1.304 (2)
C(4a)—C(10a)	1.515 (3)
C(5a)—C(9a)	1.400 (2)
C(2)—O(12)	1.216 (2)
N(3)—C(13)	1.467 (3)
C(4)—O(14)	1.215 (2)
C(4a)—C(14a)	1.571 (3)
N(5)—C(15)	1.469 (3)
C(7)—C(17)	1.511 (3)
C(8)—C(18)	1.507 (3)
N(10)—C(20)	1.467 (3)
C(14a)—C(24a)	1.493 (3)
C(24a)—C(34a)	1.305 (3)
C(6)—H(6)	0.94 (2)
C(9)—H(9)	1.01 (2)
C(13)—H(13a)	0.81 (6)
C(13)—H(13b)	0.76 (7)
C(13)—H(13c)	1.16 (6)
C(14a)—H(14a)	0.99 (2)
C(14a)—H(14b)	1.00 (3)
C(15)—H(15a)	1.03 (4)
C(15)—H(15b)	0.92 (3)
C(15)—H(15c)	1.05 (3)
C(17)—H(17a)	0.90 (3)
C(17)—H(17b)	1.01 (4)
C(17)—H(17c)	0.97 (4)
C(18)—H(18a)	1.02 (4)
C(18)—H(18b)	0.89 (4)
C(18)—H(18c)	0.94 (4)
C(20)—H(20a)	0.97 (3)
C(20)—H(20b)	1.00 (5)
C(20)—H(20c)	0.98 (4)
C(24a)—H(24)	0.91 (4)
C(34a)—H(34a)	0.94 (4)
C(34a)—H(34b)	1.00 (4)

Table 9. *Intermolecular distances less than 3.6 Å between non-hydrogen atoms*

Estimated standard deviations are given in parentheses.

Code for symmetry-related atoms

Superscript	Atom at		
None	<i>x</i> ,	<i>y</i> ,	<i>z</i>
i	$\frac{3}{2}-x$,	$1-y$,	$\frac{1}{2}+z$
ii	$1-x$,	$-\frac{1}{2}+y$,	$\frac{3}{2}-z$
iii	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1-z$

N(1)···C(13 ⁱ)	3.561 (3) Å
O(12)···C(2 ⁱ)	3.519 (3)
O(12)···N(3 ⁱ)	3.260 (3)
O(12)···C(4 ⁱ)	3.535 (3)
O(12)···C(13 ⁱ)	3.556 (2)
O(12)···C(14a ⁱ)	3.417 (2)
O(14)···C(9 ⁱⁱ)	3.297 (2)
O(14)···C(17 ⁱⁱⁱ)	3.327 (3)

109.4°, close to the ideal value 109.5° for tetrahedral atoms, and the four intramolecular bonds (*cf.* Table 7) involving C(4a) have single-bond lengths. Calculation of least-squares planes (labelled II, III and IV in Table 10) through the three six-membered rings of the isoalloxazine ring system reveals that the pyrimidinoid (II) and benzenoid (IV) rings are almost planar, while the pyrazinoid (III) ring deviates significantly from planarity. The relative orientation of these three planes

Table 10. *Deviations of the atoms from least-squares planes*

The planes are of the form $AX+BY+CZ=D$, where X , Y , and Z are in Å units relative to the axes a , b and c . The atoms indicated with asterisks were omitted from the calculations of the least-squares planes.

Deviation from plane I		Deviation from plane II	
N(1)	0.166 Å	N(1)	0.014 Å
C(2)	0.136	C(2)	-0.074
N(3)	0.024	N(3)	0.033
C(4)	-0.232	C(4)	0.052
C(4a)	-0.455	C(4a)	-0.102
N(5)	0.253	C(10a)	0.076
C(5a)	0.136	*O(12)	-0.181
C(6)	0.172	*C(13)	0.071
C(7)	0.065	*O(14)	0.146
C(8)	-0.146	*C(14a)	-1.585
C(9)	-0.177	*N(5)	0.847
C(9a)	-0.003	*N(10)	0.250
N(10)	0.089		
C(10a)	-0.028		
*O(12)	0.267		
*C(13)	0.134		
*O(14)	-0.322		
*C(14a)	-2.004		
*C(15)	1.638		
*C(17)	0.138		
*C(18)	-0.335		
*C(20)	0.362		
*C(24a)	-2.597		
*C(34a)	-3.102		

Deviation from plane III		Deviation from plane IV	
C(4a)	-0.311 Å	C(5a)	-0.014 Å
N(5)	0.254	C(6)	-0.009
C(5a)	-0.016	C(7)	0.022
C(9a)	-0.153	C(8)	-0.011
N(10)	0.097	C(9)	-0.011
C(10a)	0.129	C(9a)	0.024
*N(1)	0.465	*N(5)	-0.041
*C(4)	0.075	*N(10)	0.148
*C(6)	-0.137	*C(17)	0.053
*C(9)	-0.476	*C(18)	-0.046
*C(14a)	-1.880		
*C(15)	1.664		
*C(20)	0.370		

Plane	A	B	C	D	Root mean square deviation of the atoms without asterisks from the planes
I	0.075	-0.470	0.879	3.870	0.186 Å
II	-0.056	-0.606	0.793	1.090	0.066
III	0.201	-0.455	0.867	4.985	0.187
IV	0.026	-0.358	0.933	4.443	0.016

can be seen in Fig. 3. Thus, the molecule is slightly twisted along its elongation, due to the presence of the tetrahedral C(4a) atom. The angle between the normals to the least squares-planes of the benzenoid and pyrazinoid rings is 12.1°, and that for the pyrazinoid-pyrimidinoid pair is 17.7°.

To visualize the bond scheme consistent with the intramolecular bond distances obtained, approximate π -bond orders were evaluated (Table 11) from the linear π -bond order - bond distance correlation functions suggested by *e.g.* Ross & Skancke (1967) and Fischer-Hjalmars & Sundbom (1968): $d = A - p \times 0.180$ (where p is the bond order, d the corresponding bond distance in Å, and A is a constant which has been determined to be 1.517 Å for C-C, 1.458 Å for C-N and 1.368 Å for C-O bonds). These functions have been originally developed to evaluate bond distances from π -bond orders obtained from semi-empirical molecular orbital calculations of the Pariser-Parr-Pople type on strictly planar molecules. Since the molecules in this study are nonplanar, the bond orders given in Table 11 should be treated only as rough estimates. However, the bond order values obtained agree fairly well with the commonly accepted π -bond scheme (*cf.* Fig. 1) for

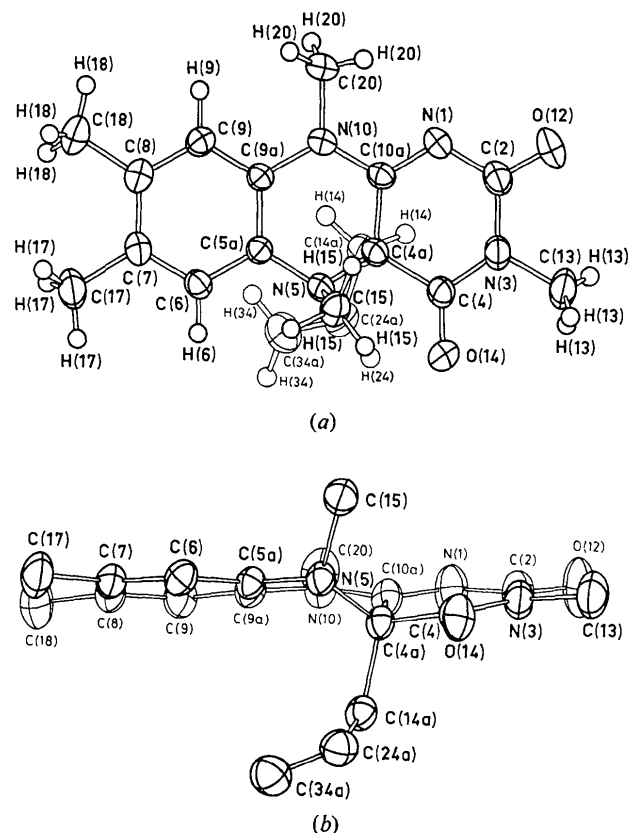


Fig. 3. Conformation of 4a-allyl-3,5,7,8,10-pentamethyl-4a,5-dihydroisoalloxazine, as seen (a) perpendicularly to, and (b) parallel to the molecular plane, with the atoms numbered for reference in the text. The non-hydrogens are represented by their thermal ellipsoids.

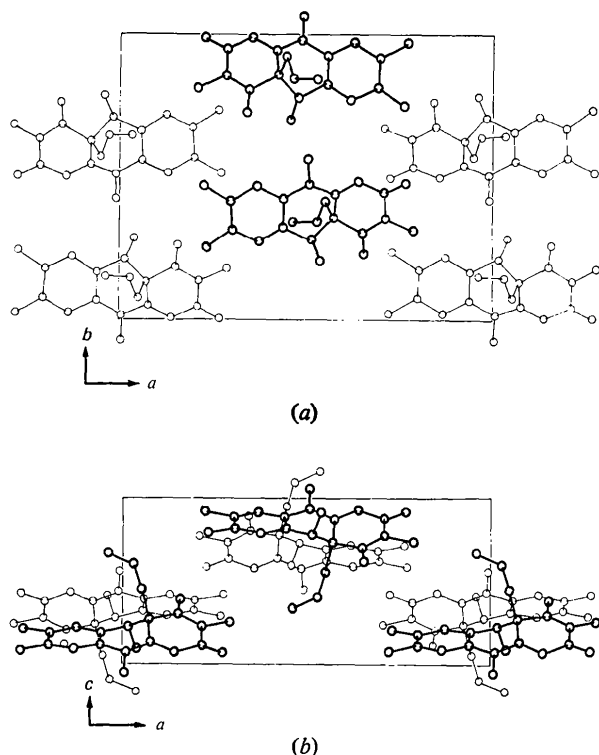


Fig. 4. Packing diagram, excluding hydrogens, projected (a) on the *ab* plane and (b) on the *ac* plane.

a fully reduced 4a,5-dihydroisoalloxazine ring system in the neutral state.

From the bond orders in Table 11, the π electrons of the benzenoid ring appear completely delocalized; bond orders range from 0.59 for the C(7)–C(8) bond to 0.72. In the pyrazinoid ring the N(10)–C(10a) bond has a fairly high (0.62) bond order. In the pyrimidinoid ring the highest bond order (0.86) is obtained for the C(10a)–N(1) bond. Fairly high bond orders, 0.47 and 0.49, also occur for the N(1)–C(2) and N(3)–C(4) bonds in this ring. The two oxygens, O(12) and O(14), attached to this ring are obviously keto, since the two

Table 11. Estimated intramolecular π bond orders, obtained from linear bond order–bond distance correlation functions

Bond	Bond order	Bond	Bond order
N(1)–C(2)	0.47	C(10a)–N(1)	0.86
C(2)–N(3)	0.27	C(4a)–C(10a)	0.00
N(3)–C(4)	0.49	C(5a)–C(9a)	0.65
C(4)–C(4a)	0.00	C(2)–O(12)	0.85
C(4a)–N(5)	0.00	N(3)–C(13)	0.00
N(5)–C(5a)	0.21	C(4)–O(14)	0.85
C(5a)–C(6)	0.71	C(4a)–C(14a)	0.00
C(6)–C(7)	0.72	N(5)–C(15)	0.00
C(7)–C(8)	0.59	C(7)–C(17)	0.00
C(8)–C(9)	0.72	C(8)–C(18)	0.06
C(9)–C(9a)	0.72	N(10)–C(20)	0.00
C(9a)–N(10)	0.19	C(14a)–C(24a)	0.13
N(10)–C(10a)	0.62	C(24a)–C(34a)	1.18

bond orders for the bonds C(2)–O(12) and C(4)–O(14) are both 0.85. Thus, there seems to be some delocalization of π electrons over the region N(10)–C(10a)–N(1)–C(2)–O(12), since all the involved bond orders deviate appreciably from zero. As discussed above, the bonds involving the carbon atom C(4a) are almost pure single bonds, as is evident from Table 11.

The geometry of the allyl group attached to the carbon atom C(4a) of the isoalloxazine ring agrees reasonably with that obtained by Dragonette & Karle (1965) in the structure of allylthiourea, as regards the bond lengths 1.305 (3) and 1.493 (3) Å for the C(34a)–C(24a) and C(24a)–C(14a) bonds, and 124.2 (2) and 114.8 (2)° for the angles C(34a)–C(24a)–C(14a) and C(24a)–C(14a)–C(4a). Thus, Dragonette & Karle obtained the values 1.27 (1) and 1.53 (1) Å for the corresponding bonds, and 128 (1)° and 113 (1)° for the angles.

The bond C(14a)–C(4a) between the allyl group and the isoalloxazine ring is 1.571 (3) Å, whereas a usual C–C single bond is 1.54 Å (Sutton, 1958). Similarly, in the structure of 5-ethyl-3,7,8,10-tetramethylisoalloxazinium perchlorate (Norrestam & Tillberg, 1972), the bond between the carbon atom of an ethyl group and the nitrogen N(5) of the isoalloxazine ring is 1.529 (6) Å, compared with the usual C–N single bond length 1.48 Å (Sutton, 1958). These long bond lengths suggest that the bonds between the alkyl groups and the isoalloxazine rings are weakened in these two derivatives. It has also been shown, in investigations (*cf.* Hemmerich, Ghisla, Hartmann & Müller, 1971) of the chemistry of different alkyldihydroisoalloxazines, that one characteristic feature is the ease of addition and removal of the alkyl substituents. This feature is, of course, relevant to the possible role of alkyldihydroisoalloxazines as intermediates in group transfer processes involving flavin enzymes.

The author is indebted to Professor Peder Kierkegaard for his active and stimulating interest in this work, and for all facilities placed at his disposal. Thanks are also due to Dr S. Ghisla for the supply of the crystals used in this work, to Dr M. von Glehn for assistance with some of the computations and to Dr Don Koenig for valuable comments on the manuscript and for his correction of the English of this paper.

This investigation has been performed with financial support from the Tri-Centennial Fund of the Bank of Sweden and from the Swedish Natural Science Research Council.

References

- BÜRGI, H. B. & DUNITZ, J. D. (1971). *Acta Cryst.* A27, 117.
 DRAGONETTE, K. S. & KARLE, I. L. (1965). *Acta Cryst.* 19, 978.
 EHRENBERG, A. & HEMMERICH, P. (1968). In *Biological Oxidations*. New York: Interscience Publishers.
 FISCHER-HJALMARS, I. & SUNDBOM, M. (1968). *Acta Chem. Scand.* 22, 607.

- GAVRON, H. (1963). *Nature, Lond.* **194**, 1270.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
 HAUPTMAN, H. (1964). *Acta Cryst.* **17**, 1421.
 HEMMERICH, P., GHISLA, S., HARTMANN, U. & MÜLLER, F. (1971). In *Flavins and Flavoproteins*. Baltimore: University Park Press.
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
 JEFCOATE, C. R., GHISLA, S. & HEMMERICH, P. (1971). *J. Chem. Soc. (C)*, p. 1689.
 KIERKEGAARD, P., NORRESTAM, R., WERNER, P.-E., CSÖREGH, I., VON GLEHN, M., KARLSON, R., LEIJONMARCK, M., RÖNNQUIST, O., STENSLAND, B., TILLBERG, O. & TORBJÖRNSSON, L. (1971). In *Flavins and Flavoproteins*. Baltimore: University Park Press.
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
 NORRESTAM, R. (1972). *Acta Cryst.* **A28**. In the press.
 NORRESTAM, R., VON GLEHN, M., HAGMAN, L.-O. & KIERKEGAARD, P. (1969). *Acta Chem. Scand.* **23**, 2199.
 NORRESTAM, R. & STENSLAND, B. (1972). *Acta Cryst.* **B28**, 440.
 NORRESTAM, R. & TILLBERG, O. (1972). *Acta Cryst.* **B28**, 890.
 ROOS, B. & SKANCKE, P. N. (1967). *Acta Chem. Scand.* **21**, 233.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configuration of Molecules and Ions*. London: The Chemical Society.
 WALKER, W. H., HEMMERICH, P. & MASSEY, V. (1967). *Helv. Chim. Acta* **50**, 2269.

Acta Cryst. (1972). **B28**, 1720

Structure d'un Dérivé de la Pyrazoline-1

PAR MARIE-PAULE ROUSSEAU, JACQUELINE MEUNIER-PIRET, JEAN-PAUL PUTZEYS, GABRIEL GERMAIN
 ET MAURICE VAN MEERSSCHE

*Laboratoire de Chimie-Physique et de Cristallographie, Université de Louvain,
 Schapenstraat 39, 3000 Louvain, Belgique*

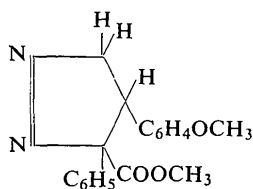
(Reçu le 1 décembre 1971)

trans-3-Phényl-3-méthoxycarbonyl-4-*p*-méthoxyphényl-1-pyrazoline cristallise dans le groupe spatial $P2_1/c$ avec $Z=4$. Les constantes de la cellule unitaire sont $a=14,183$, $b=5,777$, $c=22,681$ Å et $\beta=120,20^\circ$. Le cycle pyrazoline n'est pas planaire: l'atome de carbone C(4) est hors (0,5 Å) du plan des autres atomes du hétérocycle. La longueur de la double liaison N=N est 1,240 Å.

Introduction

Les diphenyl-3,4, carbométhoxy-3, pyrazoline-1 *cis* et *trans* substituées au niveau des phényles sont obtenues par addition de diazométhane sur la double liaison centrale des acides α -phényl cinnamiques substitués. Elles se décomposent à une température légèrement supérieure à leur point de fusion; les produits obtenus sont, pour les dérivés *trans*, des cyclopropanes et, pour les dérivés *cis*, des oléfines. Aucune règle concernant le mécanisme de cette décomposition n'a pu être établie. Il semble cependant certain que la conformation des pyrazolines joue un rôle important sur la nature des produits obtenus. Dans cet ordre d'idée, nous avons envisagé l'étude de quelques pyrazolines typiques (tant *cis* que *trans*).

Dans ce travail nous déterminons la structure de la phényl-3, carbométhoxy-3, *p*-méthoxy-phényl-4, pyrazoline-1 *trans* (C₁₈H₁₈N₂O₃).



Les spectres UV et IR donnent peu de renseignements sur cette structure. Par contre, les spectres r.m.n. indiquent qu'il s'agit probablement d'une structure rigide et que le cycle pentagonal s'écarte de la planéité (Roelens, 1970).

Partie expérimentale

Les cristaux sont incolores. Ils ont la forme de prismes allongés suivant l'axe *b*, dont la base est un hexagone irrégulier. Leur point de fusion est de 138–139°. Les données cristallographiques sont les suivantes:

$a = 14,183$ Å
 $b = 5,777$
 $c = 22,681$
 $\beta = 120,20^\circ$
 $V = 1606,1$ Å³
 Groupe spatial $P2_1/c$
 $Z = 4(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3)$
 Densité calculée: 1,283 g.cm⁻³
 $F(000) = 656$.

Les paramètres de la maille, après avoir été évalués sur des films de Weissenberg, ont été déterminés avec plus de précision en mesurant, au moyen d'un diffractomètre, l'angle 2θ de quelques réflexions.