The Crystal Structure of the Acepleiadylene, s-Trinitrobenzene Complex

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The crystal is triclinic, probably $P\bar{1}$, with $Z=2$. Unit-cell constants at $-150\,^{\circ}$C are $a=8\cdot791$, $b=16\cdot055$, $c=6\cdot515$ Å, $\alpha=92\cdot87$, $\beta=102\cdot18$, $\gamma=98\cdot98^{\circ}$. The formula is $C_{16}H_{10}.C_6H_3N_3O_6$.

The structure was determined from the three-dimensional Patterson synthesis. It was refined by Fourier and differential syntheses, and finally by least-squares procedures.

Both molecules are significantly non-planar. They overlap each other with an average interplanar spacing of 3·26 Å, but a carbon–nitrogen distance of 3·20 Å and a carbon–carbon distance of 3·24 Å also occur.

Introduction

The crystal structure of acepleiadylene $C_{16}H_{10}$ (I) is disordered, and the molecular structure has not hitherto been accurately determined (Hanson, 1960). Attempts to determine molecular parameters by refining such structures are unrewarding (Pawley, 1965). A better approach is to study the molecule in a different structural environment, as was done with azulene (Hanson, 1965). Acepleiadylene forms a stable 1:1 complex with s-trinitrobenzene $C_6H_3N_3O_6$ (II), and X-ray analysis of the complex yields a reasonably good determination of the molecular structure.
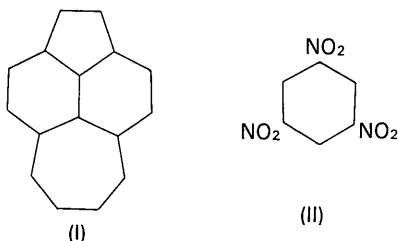
Experimental

Crystal data at $-150\,^{\circ}$C

Values in parentheses refer to measurements at room temperature.

Triclinic

$a =$	8·791	(8·798) ± 0·005 Å
$b =$	16·055	(16·202) ± 0·010
$c =$	6·515	(6·658) ± 0·005
$\alpha =$	92·87	(93·81) ± 0·05
$\beta =$	102·18	(101·93) ± 0·05
$\gamma =$	98·98	(97·65) ± 0·05°
$V =$	884	(916) Å³

Formula $C_{16}H_{10}$, $C_6H_3N_3O_6$; F.W. 415·35

$D_x = 1\cdot56$ (1·51) ± 0·01 g.cm^{-3}

$D_m = (1\cdot50) \pm 0\cdot02$ g.cm^{-3}

$Z = 2$

$\mu = 11\cdot4$ cm^{-1} (Cu $K\alpha$)

The crystal class was deduced from precession and Weissenberg photographs. The space group $P\bar{1}$ is consistent with the deduced structure.

Molecular symmetry: none.

The material crystallizes from toluene solution in the form of needles whose axes are parallel to **c**. Like acepleiadylene itself, it is deep red. A suitable specimen (a regular solid of dimensions $0\cdot2 \times 0\cdot3 \times 0\cdot4$ mm) was easily cleaved from a needle. The cell constants and the relative intensities were measured with the General Electric XRD-5 spectrogoniometer and goniostat, equipped with a scintillation counter. Copper $K\alpha$ radiation was used, and reasonable monochromatization was achieved by means of a $K\beta$ filter and a reverter (pulse-height analyser). The moving-crystal moving-counter technique of Furnas (1957) was used. Goniostat settings were precomputed and set by hand. The specimen was maintained at the working temperature of $-150\,^{\circ}$C by immersion in a stream of cold gaseous nitrogen, which was itself surrounded by an envelope of dry nitrogen at room remperature. As a safeguard against thermal shocks, it was enclosed in a thin-walled fused-quartz capillary. Of the 3953 accessible reflexions (those for which $2\theta \le 165^{\circ}$) significant counts were recorded for 3232. Absorption corrections were considered to be unnecessary. The range of observed intensity is about 1 to 20,000.

Structure determination

A trial structure was readily deduced from the three-dimensional Patterson synthesis. It was refined by means of Fourier and differential syntheses, followed by six cycles of block-diagonal least-squares analysis, using the program of Mair (1963). This program forms a 3×3 matrix for the position parameters and a 6×6 matrix (or 1×1 if thermal motion is assumed to be isotropic) for the thermal parameters of each atom. The scale factor of observed structure amplitudes and the overall isotropic temperature factor are refined in a 2×2 matrix (Cruickshank, 1961). Schomaker's cor-

Table 1. *Final parameters of non-hydrogen atoms* $\pm(x, y, z)$

Temperature factor $=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

B_i are the principal radii of the vibration ellipsoids

Atom	x $\times 10^5$	y $\times 10^5$	z $\times 10^5$	β_{11} $\times 10^5$	β_{22} $\times 10^5$	β_{33} $\times 10^5$	β_{12} $\times 10^5$	β_{13} $\times 10^5$	β_{23} $\times 10^5$	B_1 Å^2	B_2 Å^2	B_3 Å^2
					s-Trinitrobenzene							
C(1)	19141	19532	22307	443	97	708	−15	220	31	0·85	1·13	1·44
C(2)	35489	21025	27006	449	117	742	178	269	99	0·86	1·19	1·44
C(3)	42853	29391	30142	297	156	733	53	201	127	0·83	1·11	1·62
C(4)	34631	36098	28614	419	103	782	−27	269	84	0·84	1·25	1·43
C(5)	18331	34152	23533	422	110	753	153	225	77	0·90	1·21	1·34
C(6)	10192	25934	20398	301	145	691	31	150	100	0·86	1·07	1·53
N(7)	10903	10688	19468	624	112	835	−69	235	18	0·96	1·35	2·13
N(8)	60290	31290	35497	329	217	829	58	145	163	0·93	1·30	2·25
N(9)	9210	41173	21236	569	141	894	247	414	158	1·03	1·35	1·89
O(10)	−3527	9488	15424	529	180	1536	−249	129	95	0·83	2·35	3·02
O(11)	19041	5121	21740	926	87	1712	147	454	73	0·82	2·59	2·85
O(12)	67373	25269	36445	408	286	1708	328	190	305	0·89	2·61	3·13
O(13)	66494	38730	38734	435	222	1486	−221	270	77	0·83	2·38	2·97
O(14)	16608	48380	24145	881	107	1682	202	526	113	0·97	2·54	2·70
O(15)	−5191	39304	16511	442	220	1597	332	369	265	0·82	2·23	2·72
					Acepleiadylene							
C(16)	52054	60269	17141	606	122	873	−100	428	24	0·95	1·35	2·18
C(17)	68265	62708	22143	572	103	745	113	413	69	0·97	1·12	1·62
C(18)	74375	71526	25050	352	116	587	39	222	92	0·87	0·99	1·22
C(19)	91157	72647	30302	369	156	658	170	277	140	0·91	0·98	1·62
C(20)	99479	80794	33883	303	183	847	50	287	85	0·83	1·34	1·85
C(21)	90986	87513	32008	451	119	873	−80	278	33	0·86	1·40	1·74
C(22)	74417	86537	27151	464	116	725	121	329	140	0·95	1·17	1·40
C(23)	65466	78011	23258	340	125	562	104	213	109	0·84	0·92	1·27
C(24)	48444	75259	17850	333	177	717	117	241	97	0·92	1·12	1·77
C(25)	42584	66533	14993	339	209	842	−76	261	19	0·85	1·33	2·36
C(26)	81783	58344	25747	728	132	880	273	488	119	1·00	1·34	2·21
C(27)	95285	64198	30647	567	165	871	303	382	169	1·00	1·34	2·08
C(28)	67881	94244	26921	758	107	1149	148	516	160	0·98	1·79	2·18
C(29)	52593	95425	23084	936	156	1376	457	671	311	0·88	2·09	3·07
C(30)	38487	89301	17399	585	273	1360	531	396	307	0·77	2·15	3·23
C(31)	36798	80755	15050	377	266	1026	246	186	108	0·94	1·67	2·68

rection (Hodgson & Rollett, 1963) is applied to the shifts of the thermal parameters. The weighting scheme used was $1/w = 1 + \{(F_o - 5F_T)/8F_T\}^2$ where F_T is the nominal minimum observable value of F_o, in this case 3·0.

The thermal motion was assumed to be isotropic for the hydrogen atoms, and anisotropic for all others. The scattering factor curves of Freeman (1959) were used throughout. No convergence acceleration factors were applied.

As refinement continued, it became obvious that the more intense reflexions were affected by extinction, and an empirical correction curve – a plot of I_c/I_o against I_c – was devised (Pinnock, Taylor & Lipson, 1956). The curve appeared to be applicable to reflexions whose intensities are reduced by not more than 30% of the original value, and about 60 such reflexions were therefore corrected. However, the curve did *not* appear to be applicable to the three strongest reflexions (002, 11$\bar{2}$, $\bar{1}$12) whose intensities are reduced by as much as 50%. These three reflexions were left uncorrected, but were not considered in subsequent refinement. This treatment of extinction is probably unnecessary, because the weighting scheme described above discriminates strongly against the more intense

reflexions. Corrections actually applied exceeded 10% of F_o for only six reflexions.

On completion of refinement no coordinate shift of a non-hydrogen atom exceeded 0·0006 Å, or about 0·4 e.s.d.'s of atomic position. The final parameters for all atoms are given in Tables 1 and 2. It will be observed that the isotropic temperature factors for the hydrogen atoms are very small, and in some cases negative. This anomaly results from the use of an inappropriate scat-

Table 2. *Final parameters of hydrogen atoms* $\pm(x, y, z)$

Atom	x $\times 10^4$	y $\times 10^4$	z $\times 10^4$	B Å^2
H(2)	4126	1678	2813	−0·13
H(4)	3965	4158	3088	0·10
H(6)	−56	2476	1762	−0·13
H(16)	4742	5440	1513	−0·02
H(20)	1074	8190	3746	−0·42
H(21)	9672	9308	3410	0·18
H(25)	3108	6480	1163	0·07
H(26)	8147	5224	2461	0·08
H(27)	595	6277	3367	−0·42
H(28)	7588	9922	3090	−0·39
H(29)	5141	140	2381	−0·05
H(30)	2890	9166	1491	0·44
H(31)	2575	7755	1053	−0·18
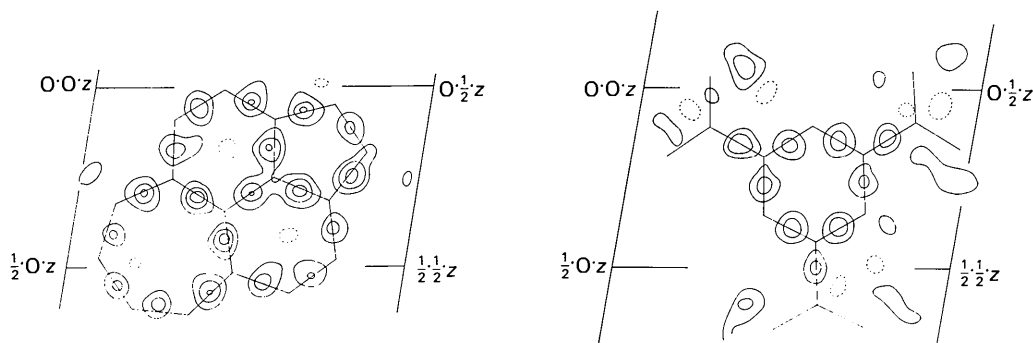
Fig. 1. Sections of ΔF synthesis in molecular planes. Solid contours are at intervals of 0·1 e.Å⁻³, the lowest being at 0·1 e.Å⁻³. The broken contour is at $-0\cdot1$ e.Å⁻³.

tering-factor curve for bonded hydrogens, and is typical.

Assessment of results

The agreement between observed and calculated structure amplitudes is reasonable, as indicated by the agreement summary (Table 3), and there can be no doubt

Fig. 2. The thermal motion ellipsoids.

of the essential correctness of the structure. It seems unnecessary to publish the table of F_o and F_c, but copies may be obtained by writing to the National Science Library, National Research Council, Ottawa, Canada, giving reference to the paper. The final agreement residual $(R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|)$ is 0·047, for observed reflexions only.

The three-dimensional difference synthesis reveals some significant detail in the neighbourhood of the molecules. Sections through the molecular planes are shown in Fig. 1. The peaks which occur at the mid points of all C–C and C–N bonds are presumably due to the presence of bonding electrons. In regions remote from the molecules, the residual electron density ranges from $-0\cdot24$ to $0\cdot20$ e.Å⁻³. The e.s.d. of electron density is 0·14 e.Å⁻³.

For carbon atoms the e.s.d. of position is about 0·0020 Å, and for nitrogen and oxygen atoms, about 0·0015 Å.

Thermal motion

Inspection of Table 1 indicates that while the thermal motion of the structure is reasonably small, it is unquestionably anisotropic. The nature of the anisotropy is illustrated in Fig. 2. For the acepleiadylene molecule the motion appears to be simply rigid-body libration about the centre of gravity, chiefly in the molecular plane. Libration corrections by the methods of Busing & Levy (1964) have the effect of lengthening all the bonds by about 0·16%. The thermal motion of the less rigid s-trinitrobenzene molecule is more complex, and defies rigorous analysis. However, the following interpretation is at least plausible. Each NO_2 group librates about two axes, one containing the adjacent C–N bond, and the other normal to the molecular plane through the adjacent carbon atom. In addition, the benzene nucleus librates (chiefly in the molecular plane) about the centre of gravity. Bond-length corrections appropriate to this speculative interpretation have been attempted, but may be unreliable for the N–O bonds. Corrections to the C–N bonds are small because it is assumed that the vibrations of these atoms are parallel, and highly correlated. Corrected and uncorrected bond lengths are given in Table 4.
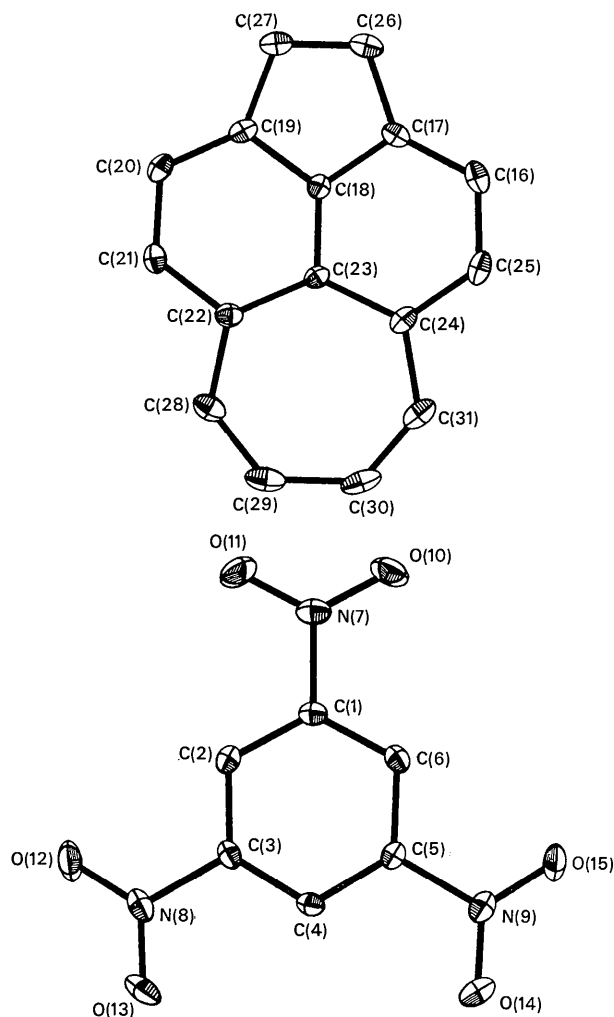
Table 3. *Agreement summary*

$\Delta F = |F_o| - |F_c|$
F_T = estimated minimum observable structure amplitude for reflexion concerned.

	Category		Number of reflexions Observed	Unobserved
1	$(|\Delta F| \leq \frac{1}{2}F_T$ or	$|\Delta F| \leq 0\cdot1 F_o)$	3088 ⎤	
2	$(\frac{1}{2}F_T < |\Delta F| \leq F_T$ or $0\cdot1 F_o < |\Delta F| \leq 0\cdot2 F_o)$		135 ⎦	644
3	$(F_T < |\Delta F| \leq \frac{3}{2}F_T$ or $0\cdot2 F_o < |\Delta F| \leq 0\cdot3 F_o)$		5	72
4	$(\frac{3}{2}F_T < |\Delta F| \leq 2F_T$ or $0\cdot3 F_o < |\Delta F| \leq 0\cdot4 F_o)$		4	5

Table 4. *Bond lengths*

Bond		l uncorrected (Å)	Δl (Å × 1000)	l corrected (Å)	Mean (Å)	Mean e.s.d. (Å × 1000)	Fraction of double-bond character
C(1)	C(2)	1·384	4	1·388 ⎤			
C(2)	C(3)	1·382	4	1·386			
C(3)	C(4)	1·384	4	1·388	1·387	3	
C(4)	C(5)	1·382	4	1·386			
C(5)	C(6)	1·382	4	1·386			
C(6)	C(1)	1·384	4	1·388 ⎦			
C(1)	N(7)	1·473	1	1·474 ⎤			
C(3)	N(8)	1·477	1	1·478	1·477	2	
C(5)	N(9)	1·478	1	1·479 ⎦			
N(7)	O(10)	1·222	10	1·232 ⎤			
N(7)	O(11)	1·225	10	1·235			
N(8)	O(12)	1·226	10	1·236	1·236	2	
N(8)	O(13)	1·221	10	1·231			
N(9)	O(14)	1·220	10	1·230			
N(9)	O(15)	1·223	10	1·233 ⎦			
C(28)	C(29)	1·359	2	1·361 ⎤	1·358	3 ⎤	
C(30)	C(31)	1·354	2	1·356 ⎦		⎦	
C(26)	C(27)	1·362	2	1·364	1·364	3	$\frac{3}{4}$
C(16)	C(17)	1·381	2	1·383 ⎤	1·382	3	
C(19)	C(20)	1·378	2	1·380 ⎦			
C(18)	C(23)	1·393	2	1·395	1·395	2	
C(16)	C(25)	1·397	2	1·399 ⎤	1·401	2	$\frac{1}{2}$
C(20)	C(21)	1·401	2	1·403 ⎦			
C(21)	C(22)	1·406	2	1·408 ⎤	1·407	3	
C(24)	C(25)	1·404	2	1·406 ⎦			
C(17)	C(18)	1·422	2	1·424 ⎤	1·424	3	
C(18)	C(19)	1·423	2	1·425 ⎦			
C(29)	C(30)	1·425	2	1·427	1·427	3	
C(22)	C(28)	1·443	2	1·445 ⎤	1·444	2	$\frac{1}{4}$
C(24)	C(31)	1·442	2	1·444 ⎦			
C(22)	C(23)	1·450	2	1·452 ⎤	1·454	3	
C(23)	C(24)	1·454	2	1·456 ⎦			
C(17)	C(26)	1·455	2	1·457 ⎤	1·458	2	
C(19)	C(27)	1·458	2	1·460 ⎦			

Discussion

Details of the molecular structures are given in Table 4 and Fig. 3. There are no significant differences between chemically equivalent bond lengths or angles for either molecule. The acepleiadylene molecule is significantly non-planar, particularly in the seven-membered ring. The bond lengths correlate fairly well with those expected on consideration of the four possible Kekulé structures (Fig. 4). However, variations within certain groups are significant.

The NO_2 groups are twisted out of the mean plane of the s-trinitrobenzene molecule in typical fashion. Even the benzene nucleus is significantly non-planar, and the reason for this can be seen by considering the atomic positions with respect to the reference plane through C(2), C(4), and C(6). N(7) and N(9) are dis-

placed considerably from this plane (presumably because of packing requirements) and the bonded carbon atoms C(1) and C(5) follow them. N(8) however is only slightly displaced, and C(3) remains in the plane.

Both molecules are practically parallel to the plane normal to c and thus, to each other. They overlap each other as shown in Fig. 5, with an average interplanar spacing of $c/2$, or 3·26 Å. It is particularly to be noted that the non-substituted carbon atoms C(2), C(4) and C(6) of the s-trinitrobenzene molecule are almost precisely overlapped by atoms of the acepleiadylene molecule. This configuration has been observed for the complexes of s-trinitrobenzene with skatole and indole (Hanson, 1964). It does not occur in the complex with azulene which (perhaps for this reason) is a comparatively weak one (Hanson, 1965). Smallest intermolecular distances involving the non-substituted carbon
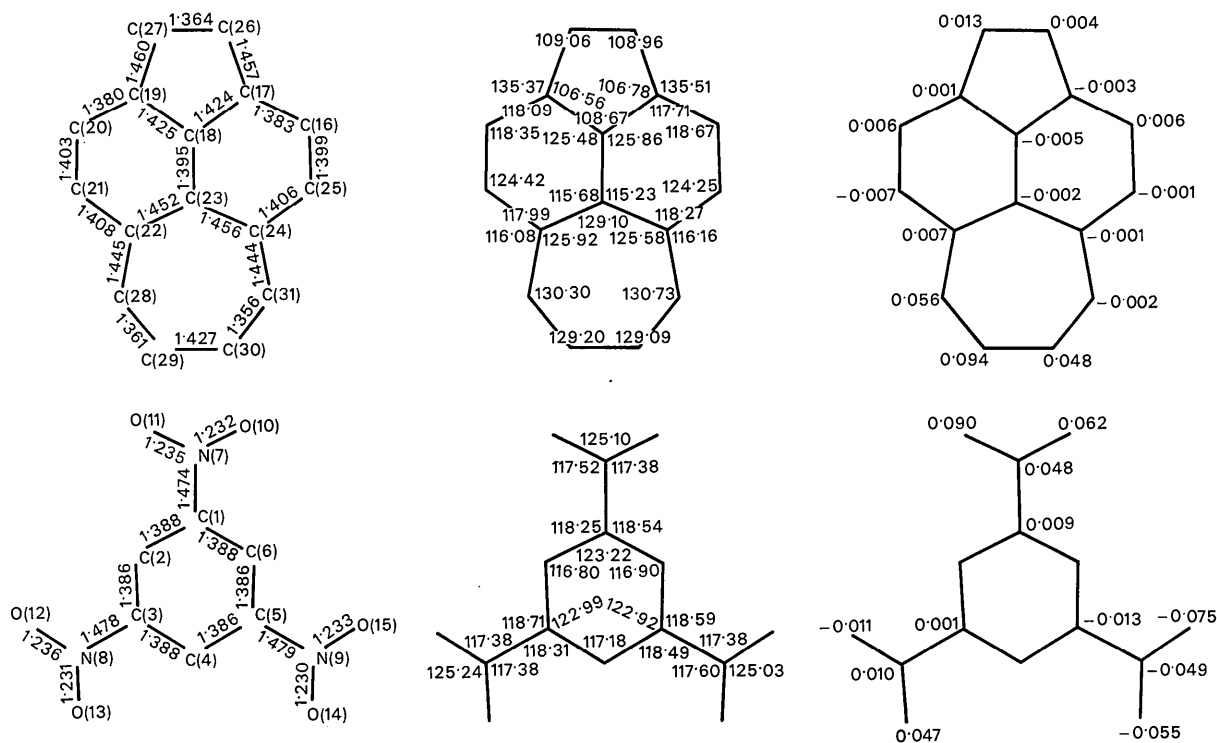

Fig. 3. Bond lengths, angles, and departures from planarity (Å). For the acepleiadylene molecule the reference plane is the mean plane of the naphthalene nucleus. For the s-trinitrobenzene molecule the reference plane contains C(2), C(4), and C(6).
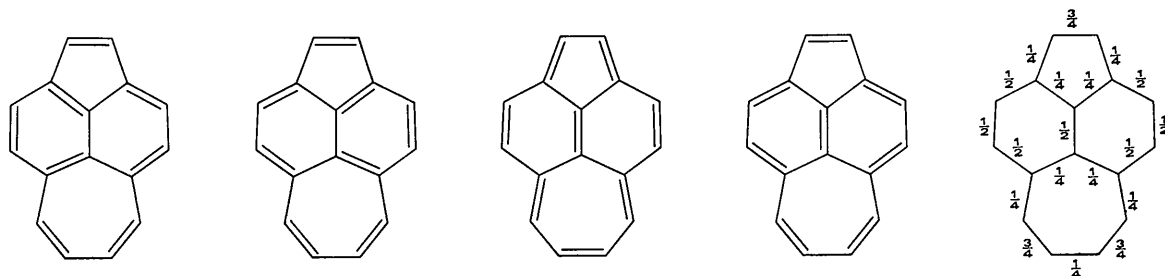

Fig. 4. The four Kekulé struxtures, and the corresponding fractions of double-bond character.

atoms are 3·24 Å [C(6)–C'(19)], 3·26 Å [C(2)–C'(23)] and 3·27 Å [C(4)–C'(17)]. Other short distances between overlapping molecules are 3·20 Å [N(7)–C'(21)] and 3·29 Å [N(8)–C'(25)]. The smallest distances between non-overlapping molecules are typical van der Waals values: 3·06 Å for oxygen–oxygen; 3·31 Å for carbon–oxygen; 3·39 Å for carbon–carbon.

It was not expected that the hydrogen positions would be established with sufficient accuracy to warrant discussion of the carbon–hydrogen bond lengths. However, the values observed are surprisingly consistent. The ten values for the acepleiadylene molecule range from 0·94 to 1·00 Å, with a standard deviation of 0·016 Å from a mean of 0·97 Å. The three values for the s-trinitrobenzene molecule are all 0·91 Å (with, formally, no standard deviation at all, but probably with the same inherent accuracy). The difference between the mean values is pointed out as an unexpected and possibly significant anomaly.

Fig. 2 was taken from the atlas of stereoscopic drawings prepared by Dr C. K. Johnson of the Oak Ridge National Laboratory for the Joint Meeting of the A.C.A. and M.S.A. at Gatlinburg, Tennessee, June 27-July 2 1965. Other computations were carried out on the IBM 1620 computer, using the programs of Dr F. R. Ahmed, Dr G. A. Mair, Mrs M. E. Pippy, and Dr S. R. Hall. The assistance of those mentioned and the continued encouragement of Dr W. H. Barnes, are gratefully acknowledged.

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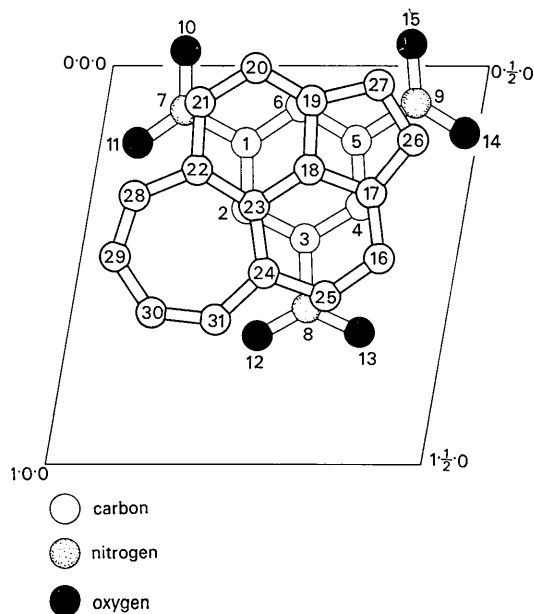PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1956). Acta Cryst. 9, 173.

Fig. 5. Projection along c of asymmetric unit, showing overlap.