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4,5,10,11,12,13-Hexahydro-10,13a-methanocycloocta[*c*]pyrrolo[3,2,1-*ij*]quinoline-7,9,14-trione and Dimethyl 4,5,10,11,12,12a-Hexahydroindolo[1,7-*cd*]benzazepine-7,8-dicarboxylate

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The trione $C_{18}H_{15}NO_3$ is monoclinic, $P2_1/n$, with a = 7·340 (1), b = 11·647 (1), c = 16·100 (3) Å, γ = 80·96 (1)°, Z = 4, D_m = 1·43, D_c = 1·432 g cm^{-3}, μ = 1·056 cm^{-1} (Mo $K\alpha$ radiation). The diester $C_{20}H_{21}NO_4$ is triclinic, $P\bar{1}$, with a = 9·605 (2), b = 9·693 (2), c = 9·871 (3) Å, α = 100·49 (2), β = 108·47 (2), γ = 99·34 (2)°, Z = 2, D_m = 1·39, D_c = 1·393 g cm^{-3}, μ = 0·99 cm^{-1} (Mo $K\alpha$ radiation). The identification of these compounds by X-ray analysis has led to an understanding of the reaction between 1,2,6,7,8,9-hexahydropyrrolo[3,2,1-*jk*]carbazole and dimethyl acetylenedicarboxylate in acetic acid.

Introduction

The synthesis and isolation of these compounds was carried out by Dr R. M. Letcher (Acheson, Letcher & Procter, 1978).

Precession photographs gave the space groups. The crystals were transferred to an Enraf–Nonius CAD-4 four-circle diffractometer, and cell dimensions determined by a least-squares fit to the setting angles of 25 reflections measured on both sides of the incident beam. The data were collected by an $\omega/2\theta$ scan, and standards checked every hour. Details of the data and R factors appear in Table 1. Lorentz and polarization corrections were applied. The structures were solved with *MULTAN* (Germain, Main & Woolfson, 1971), and refined by full-matrix least squares to $R = R(1)$ with isotropic temperature factors. Further refinement with anisotropic thermal motion to $R = R(2)$, followed by a difference synthesis, led to the location of all the H atoms [except for H(163) in the trione (IV) which was placed by calculation]. The structures were refined to

Table 1. *Experimental data and R values*

	Compound (IV)*†	Compound (V)†
Crystal dimensions (mm)	0·3 × 0·3 × 0·4	0·4 × 0·5 × 0·8
Crystallization solvent	Ethyl acetate	CH_2Cl_2/petrol
Radiation	Mo $K\alpha$	Mo $K\alpha$
Maximum 2θ (°)	44	60
Total unique data	1561	3756
Data with $I \geq 3\sigma(I)$	1416	2974‡
R(1)	0·189	0·153
R(2)	0·088	0·048
Final R	0·035	0·046

Weighting scheme: $w = [a_0t_0(x) + a_1t_1(x) + \ldots + a_nt_n(x)]^{-1}$, where a_i are coefficients of a Chebyshev series in $t_i(x)$, $(x) = F_o/F_{(\max)}$.
Final parameters: (IV): a_0 = 47·77, a_1 = 78·12, a_2 = 42·82, a_3 = 15·26, a_4 = 3·14, a_5 = 0·16; (V): a_0 = 71·10, a_1 = 97·10, a_2 = 27·53.

* C—H distances constrained to be 1·00 ± 0·01 Å.

† An extinction correction was applied during the later refinements.

‡ In the final refinements, three reflections were omitted because they suffered excessive extinction.

Table 2. *Final atomic coordinates for the trione* (IV) *with e.s.d.'s in parentheses*

	x	*y*	*z*
C(1)	0·2309 (2)	0·8513 (2)	0·0960 (1)
C(2)	0·2147 (3)	0·8296 (2)	0·0116 (1)
C(3)	0·2260 (3)	0·9156 (2)	−0·0467 (1)
C(3a)	0·2505 (2)	1·0247 (2)	−0·0206 (1)
C(4)	0·2640 (3)	1·1350 (2)	−0·0667 (1)
C(5)	0·2859 (3)	1·2242 (2)	0·0010 (1)
N(6)	0·2901 (2)	1·1579 (1)	0·07938 (9)
C(6a)	0·2664 (2)	1·0431 (2)	0·0635 (1)
C(7)	0·3447 (3)	1·1946 (2)	0·1525 (1)
C(7a)	0·3639 (2)	1·1050 (1)	0·2208 (1)
C(8)	0·4601 (3)	1·1279 (2)	0·2873 (1)
C(9)	0·4907 (3)	1·0509 (2)	0·3590 (1)
C(10)	0·4003 (3)	0·9434 (2)	0·3572 (1)
C(11)	0·2037 (3)	0·9686 (2)	0·3949 (1)
C(12)	0·0749 (3)	1·0563 (2)	0·3438 (1)
C(13)	0·0749 (2)	1·0214 (2)	0·2530 (1)
C(13a)	0·2734 (2)	0·9961 (1)	0·2138 (1)
C(13b)	0·2594 (2)	0·9602 (1)	0·1241 (1)
C(14)	0·3824 (2)	0·9036 (1)	0·2694 (1)
O(1)	0·3805 (2)	1·2927 (1)	0·1631 (1)
O(2)	0·5821 (2)	1·0742 (1)	0·41789 (9)
O(3)	0·4429 (2)	0·8067 (1)	0·24680 (9)
H(11)	0·224 (2)	0·787 (1)	0·1362 (9)
H(21)	0·199 (3)	0·750 (1)	−0·005 (1)
H(31)	0·219 (3)	0·899 (2)	−0·1071 (6)
H(41)	0·370 (2)	1·126 (2)	−0·106 (1)
H(42)	0·152 (2)	1·162 (2)	−0·101 (1)
H(51)	0·179 (2)	1·288 (1)	0·004 (1)
H(52)	0·405 (2)	1·255 (2)	−0·001 (1)
H(81)	0·514 (2)	1·201 (1)	0·289 (1)
H(101)	0·476 (2)	0·881 (1)	0·390 (1)
H(111)	0·214 (3)	0·997 (2)	0·4527 (7)
H(112)	0·155 (2)	0·894 (1)	0·394 (1)
H(121)	0·111 (2)	1·135 (1)	0·348 (1)
H(122)	−0·054 (2)	1·063 (2)	0·366 (1)
H(131)	0·002 (2)	1·084 (1)	0·219 (1)
H(132)	0·024 (2)	0·947 (1)	0·247 (1)

convergence by blocked-matrix least squares. Tables 2, 3, 4 and 5 list the final atomic coordinates, bond distances, and bond angles.* The molecular geometries of the title compounds are shown in Figs. 1 and 2. All calculations were performed on the Oxford University Computing Laboratory's ICL 1906A computer with the *CRYSTALS* package (Carruthers, 1975).

Discussion

Table 3. *Final atomic coordinates for the diester* (V) *with e.s.d.'s in parentheses*

	x	*y*	*z*
C(1)	1·0790 (2)	0·0951 (2)	0·7583 (2)
C(2)	0·9618 (2)	0·1003 (2)	0·8104 (2)
C(3)	0·8494 (2)	0·1675 (2)	0·7483 (2)
C(3a)	0·8570 (2)	0·2270 (2)	0·6335 (2)
C(4)	0·7501 (2)	0·3056 (2)	0·5516 (2)
C(5)	0·8014 (2)	0·3235 (2)	0·4240 (2)
N(6)	0·9490 (1)	0·2841 (1)	0·4577 (1)
C(6a)	0·9756 (2)	0·2208 (1)	0·5404 (2)
C(7)	1·0270 (2)	0·2941 (2)	0·3643 (2)
C(8)	1·1736 (2)	0·2888 (2)	0·3941 (2)
C(8a)	1·2702 (2)	0·2796 (2)	0·5405 (2)
C(9)	1·3927 (2)	0·3825 (2)	0·6241 (2)
C(10)	1·4979 (2)	0·3793 (2)	0·7725 (2)
C(11)	1·4418 (2)	0·2518 (2)	0·8276 (2)
C(12)	1·3620 (2)	0·1183 (2)	0·7003 (2)
C(12a)	1·2228 (2)	0·1448 (2)	0·5888 (2)
C(12b)	1·0917 (2)	0·1554 (2)	0·6423 (2)
C(13)	0·9294 (2)	0·3100 (2)	0·2157 (2)
C(14)	0·8493 (2)	0·4791 (2)	0·0833 (2)
C(15)	1·2284 (2)	0·2736 (2)	0·2701 (2)
C(16)	1·3936 (3)	0·1744 (3)	0·1713 (2)
O(1)	0·8416 (2)	0·2108 (1)	0·1191 (1)
O(2)	0·9450 (1)	0·4482 (1)	0·2149 (1)
O(3)	1·1722 (2)	0·3037 (2)	0·1550 (1)
O(4)	1·3487 (1)	0·2149 (2)	0·2961 (1)
H(11)	1·154 (2)	0·050 (2)	0·802 (2)
H(21)	0·960 (2)	0·058 (2)	0·891 (2)
H(31)	0·767 (2)	0·173 (2)	0·786 (2)
H(41)	0·647 (3)	0·255 (3)	0·515 (3)
H(42)	0·758 (2)	0·401 (2)	0·619 (2)
H(51)	0·729 (3)	0·251 (3)	0·326 (3)
H(52)	0·814 (2)	0·424 (2)	0·413 (2)
H(91)	1·419 (2)	0·463 (2)	0·586 (2)
H(101)	1·597 (2)	0·381 (2)	0·768 (2)
H(102)	1·513 (3)	0·471 (3)	0·847 (3)
H(111)	1·526 (3)	0·230 (2)	0·896 (3)
H(112)	1·370 (2)	0·273 (2)	0·879 (2)
H(121)	1·332 (2)	0·032 (2)	0·737 (2)
H(122)	1·426 (2)	0·059 (2)	0·650 (2)
H(12a1)	1·183 (2)	0·062 (2)	0·498 (2)
H(141)	0·857 (3)	0·416 (3)	−0·005 (3)
H(142)	0·746 (3)	0·444 (3)	0·078 (3)
H(143)	0·880 (3)	0·577 (3)	0·100 (3)
H(161)	1·467 (4)	0·112 (3)	0·200 (3)
H(162)	1·307 (3)	0·112 (3)	0·087 (3)
H(163)	1·437 (4)	0·261 (4)	0·153 (4)

1,2,6,7,8,9-Hexahydropyrrolo[3,2,1-*jk*]carbazole (I) with dimethyl acetylenedicarboxylate in acetic acid gave four crystalline compounds, the structures of which could not be decided from their mass, UV, IR, ^{1}H NMR, and ^{13}C NMR spectra (Acheson, Letcher & Procter, 1978). From our X-ray determinations two can be represented by (IV) and (V). Their formation from (I) necessitates the opening of the pyrrole ring, formally a hydrolysis of an enaminic system, to aminoketone derivatives such as (II) and (III). This is in effect the hydrolysis of an indole to the corresponding aminoketone, almost the reverse of the last stage of the Fischer indole synthesis (Acheson, 1976) and a very uncommon reaction. The hydrolysis of (I) to (II) can be attributed to the relief of the strain caused by the bridging ethano group (Blake, Tretter, Juhasz, Bonthrone & Rapoport, 1966). The trione (IV) could be formed from (III), and (V) from (II).

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* Lists of structure factors and thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33360 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Interatomic distances* (Å) *with e.s.d.'s in parentheses*

The trione (IV)*		The diester (V)†	
C(1)–C(2)	1·390 (3)	C(1)–C(2)	1·382 (3)
C(1)–C(13b)	1·392 (3)	C(1)–C(13b)	1·405 (2)
C(1)–H(11)	0·996 (9)	C(1)–H(11)	0·938 (20)
C(2)–C(3)	1·385 (3)	C(2)–C(3)	1·385 (3)
C(2)–H(21)	0·994 (9)	C(2)–H(21)	0·964 (20)
C(3)–C(3a)	1·377 (3)	C(3)–C(3a)	1·378 (2)
C(3)–H(31)	0·994 (9)	C(3)–H(31)	0·978 (20)
C(3a)–C(4)	1·500 (3)	C(3a)–C(4)	1·497 (2)
C(3a)–C(6a)	1·379 (3)	C(3a)–C(6a)	1·402 (2)
C(4)–C(5)	1·530 (4)	C(4)–C(5)	1·518 (3)
C(4)–H(41)	0·997 (9)	C(4)–H(41)	0·949 (25)
C(4)–H(42)	0·996 (9)	C(4)–H(42)	1·016 (22)
C(5)–N(6)	1·478 (3)	C(5)–N(6)	1·480 (2)
C(5)–H(51)	0·995 (9)	C(5)–H(51)	1·043 (24)
C(5)–H(52)	1·000 (9)	C(5)–H(52)	0·989 (23)
N(6)–C(6a)	1·399 (2)	N(6)–C(6a)	1·426 (2)
N(6)–C(7)	1·336 (2)	N(6)–C(7)	1·367 (2)
C(6a)–C(13b)	1·379 (3)	C(6a)–C(12b)	1·399 (2)
C(7)–C(7a)	1·507 (3)	C(7)–C(8)	1·356 (2)
C(7)–O(1)	1·225 (2)	C(7)–C(13)	1·520 (2)
C(7a)–C(8)	1·332 (3)	C(8)–C(8a)	1·477 (2)
C(7a)–C(13a)	1·526 (2)	C(8)–C(15)	1·471 (2)
C(8)–C(9)	1·458 (3)	C(8a)–C(9)	1·328 (2)
C(8)–H(81)	0·992 (9)	C(8a)–C(12a)	1·521 (2)
C(9)–C(10)	1·506 (3)	C(9)–C(10)	1·502 (2)
C(9)–O(2)	1·217 (2)	C(9)–H(91)	0·961 (19)
C(10)–C(11)	1·550 (3)	C(10)–C(11)	1·525 (3)
C(10)–C(14)	1·500 (3)	C(10)–H(101)	0·962 (21)
C(10)–H(101)	0·994 (9)	C(10)–H(102)	1·006 (24)
C(11)–C(12)	1·520 (3)	C(11)–C(12)	1·522 (3)
C(11)–H(111)	0·994 (9)	C(11)–H(111)	0·959 (23)
C(11)–H(112)	0·993 (9)	C(11)–H(112)	1·002 (20)
C(12)–C(13)	1·517 (3)	C(12)–C(12a)	1·532 (2)
C(12)–H(121)	0·999 (3)	C(12)–H(121)	1·010 (20)
C(12)–H(122)	1·000 (9)	C(12)–H(122)	0·939 (20)
C(13)–C(13a)	1·573 (2)	C(12a)–C(12b)	1·523 (2)
C(13)–H(131)	0·997 (9)	C(12a)–H(12a1)	1·012 (18)
C(13)–H(132)	0·998 (9)	C(13)–O(1)	1·199 (2)
C(13a)–C(13b)	1·511 (2)	C(13)–O(2)	1·325 (2)
C(13a)–C(14)	1·528 (2)	C(14)–O(2)	1·448 (2)
C(14)–O(3)	1·202 (2)	C(15)–O(3)	1·205 (2)
		C(15)–O(4)	1·343 (2)
		C(16)–O(4)	1·440 (2)

* C–H distances constrained to 1·00 ± 0·01 Å.

† Ester methyl C–H distances in the range 0·910 (27)–1·014 (33) Å.

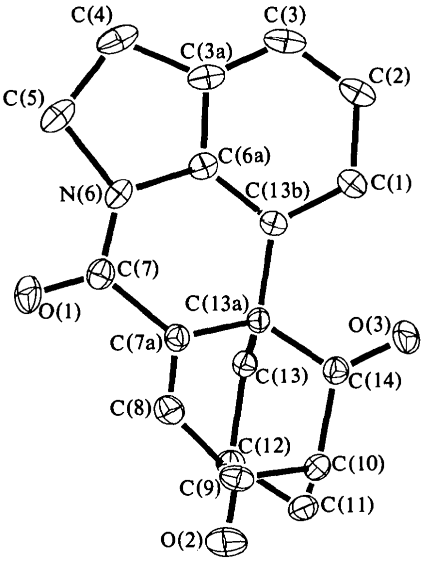


Fig. 1. Molecular geometry for the trione (IV) with H atoms omitted.

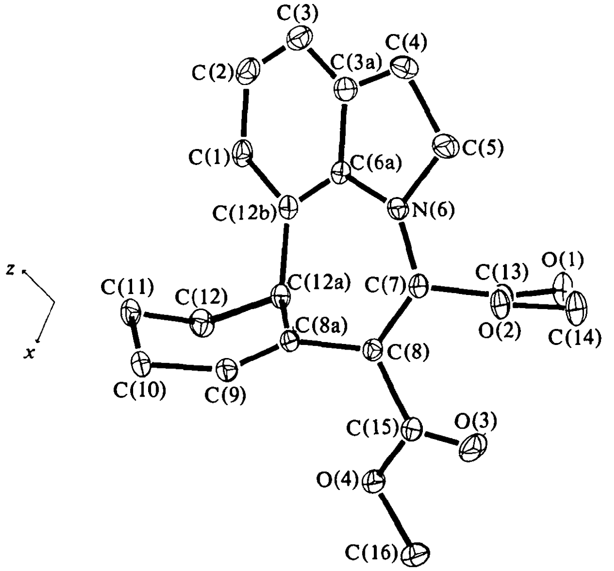
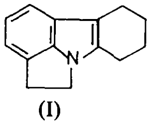
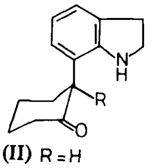


Fig. 2. Molecular geometry for the diester (V) with H atoms omitted.



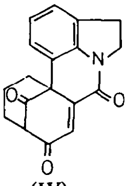
(I)

$E = CO_2CH_3$

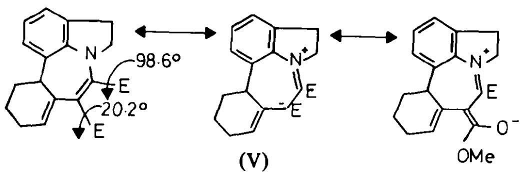


(II) R = H

(III) R = $\overset{E}{\diagup}C = C\overset{H}{\diagdown}_{E}$



(IV)



(V)

The ^{13}C NMR spectrum of (IV) shows one CH_2 resonance at surprisingly high field, 16·7*δ*, *ca* 10 p.p.m. higher than the methylene C atoms of cyclohexanone (Johnson & Jankowski, 1972). This resonance is assigned to C(12), since this atom is unique in being joined by short bonds to both neighbouring C atoms. Such upfield shifts have been observed (Wehrli & Wirthlin, 1976) in systems with short non-bonded H···H interactions, but these are absent in (IV).

Table 5. *Bond angles* (°) *with e.s.d.'s in parentheses* (H *atoms have been omitted*)

The trione (IV)

C(2)–C(1)–C(13b)	120·80 (19)	C(7a)–C(7)–O(1)	122·27 (18)	C(12)–C(13)–C(13a)	113·44 (15)
C(1)–C(2)–C(3)	121·00 (20)	C(7)–C(7a)–C(8)	116·26 (16)	C(7a)–C(13a)–C(13)	109·04 (13)
C(2)–C(3)–C(3a)	119·42 (18)	C(7)–C(7a)–C(13a)	121·04 (15)	C(7a)–C(13a)–C(13b)	111·02 (14)
C(3)–C(3a)–C(4)	132·45 (19)	C(8)–C(7a)–C(13)	122·69 (17)	C(7a)–C(13a)–C(14)	107·14 (14)
C(3)–C(3a)–C(6a)	118·00 (19)	C(7a)–C(8)–C(9)	123·23 (18)	C(13)–C(13a)–C(13b)	109·53 (14)
C(4)–C(3a)–C(6a)	109·55 (19)	C(8)–C(9)–C(10)	116·82 (16)	C(13)–C(13a)–C(14)	105·30 (14)
C(3a)–C(4)–C(5)	104·91 (19)	C(8)–C(9)–O(2)	121·11 (19)	C(13b)–C(13a)–C(14)	114·56 (14)
C(4)–C(5)–N(6)	104·44 (17)	C(10)–C(9)–O(2)	122·06 (19)	C(1)–C(13b)–C(6a)	115·79 (16)
C(5)–N(6)–C(6a)	110·33 (16)	C(9)–C(19)–C(11)	110·72 (16)	C(1)–C(13b)–C(13)	126·08 (16)
C(5)–N(6)–C(7)	124·70 (16)	C(9)–C(10)–C(14)	110·29 (15)	C(6a)–C(13b)–C(13a)	118·06 (15)
C(6a)–N(6)–C(7)	123·75 (15)	C(11)–C(10)–C(14)	107·64 (15)	C(10)–C(14)–C(13a)	113·31 (15)
N(6)–C(7)–C(7a)	114·96 (15)	C(10)–C(11)–C(12)	112·20 (15)	C(10)–C(14)–O(3)	122·59 (17)
N(6)–C(7)–O(1)	122·75 (18)	C(11)–C(12)–C(13)	111·57 (15)	C(13a)–C(14)–O(3)	124·04 (17)

The diester (V)

C(2)–C(1)–C(12b)	123·23 (16)	N(6)–C(7)–C(8)	126·02 (13)	C(8a)–C(12a)–C(12b)	110·57 (12)
C(1)–C(2)–C(3)	120·16 (15)	N(6)–C(7)–C(13)	112·29 (12)	C(12)–C(12a)–C(12b)	114·92 (13)
C(2)–C(3)–C(3a)	118·48 (16)	C(8)–C(7)–C(13)	121·68 (13)	C(1)–C(12b)–C(6a)	115·37 (14)
C(3)–C(3a)–C(4)	127·67 (15)	C(7)–C(8)–C(8a)	121·65 (13)	C(1)–C(12b)–C(12a)	120·75 (13)
C(3)–C(3a)–C(6a)	121·16 (15)	C(7)–C(8)–C(15)	117·46 (13)	C(6a)–C(12b)–C(12a)	123·87 (12)
C(4)–C(3a)–C(6a)	111·16 (14)	C(8a)–C(8)–C(15)	120·44 (13)	C(7)–C(13)–O(1)	123·65 (14)
C(3a)–C(4)–C(5)	103·48 (13)	C(8)–C(8a)–C(9)	121·71 (13)	C(7)–C(13)–O(2)	110·42 (12)
C(4)–C(5)–N(6)	106·00 (14)	C(8)–C(8a)–C(12a)	116·23 (12)	O(1)–C(13)–O(2)	125·62 (14)
C(5)–N(6)–C(6a)	109·60 (12)	C(9)–C(8a)–C(12a)	122·05 (13)	C(8)–C(15)–O(3)	125·93 (15)
C(5)–N(6)–C(7)	119·85 (13)	C(8a)–C(9)–C(10)	124·72 (15)	C(8)–C(15)–O(4)	111·98 (12)
C(6a)–N(6)–C(7)	129·97 (12)	C(9)–C(10)–C(11)	113·14 (14)	O(3)–C(15)–O(4)	122·03 (15)
C(3a)–C(6a)–N(6)	108·38 (13)	C(10)–C(11)–C(12)	110·79 (14)	C(13)–O(2)–C(14)	116·09 (13)
C(3a)–C(6a)–C(12b)	121·59 (13)	C(11)–C(12)–C(12a)	110·79 (14)	C(15)–O(4)–C(16)	115·29 (14)
N(6)–C(6a)–C(12b)	129·99 (13)	C(8a)–C(12a)–C(12)	108·68 (13)		

Table 6. *Deviations from the best plane* (Å) *for the diester* (V)

C(5)	−0·16	C(7)	0·04	C(16)	−0·38
N(6)	−0·02	C(8)	0·42	O(3)	−0·01
C(6a)	−0·14	C(15)	0·17	O(4)	0·08

In (V), the system N(6), C(7), C(8), C(15), and O(3) cannot be planar (Acheson, Procter & Critchley, 1977) because of the molecular geometry (Table 6). However, significant charge delocalization as shown is indicated by the following. The N atom is only 0·06 Å out of the plane defined by N(6), C(5), C(6a), and C(7) and the 8–CO_2 plane subtends only 20·2° with this plane. N(6)–C(7) is much shorter than the other bonds from the N atom; C(7)–C(8) is long for a double bond and C(8)–C(15) is significantly shorter than C(7)–C(13). The resonance position of C(8) in the ^{13}C NMR spectrum (108·9δ) is at high field showing increased electron density. Investigations concerning the formation and properties of (IV) and (V) will be presented later.

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