MINDO-Forces Study of α-Substituted Cyclopropyl and Isopropyl Radicals

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The structures of α-X-cyclopropyl and α-X-isopropyl radicals (X = H, O^-, OH, NH_2, CH_3, NO_2, CHO, CN, F and CF_3) are reported using MINDO-Forces MO method. In both radicals the planar structure is prefered over the pyramidal. All the substituents are stabilizing; the O^- group is the most stabilizing substituent, while F group has little effect. O^-, OH, F substituents are electron releasing groups on cyclopropyl ring, while NO_2, CHO and CF_3 are electron widthdrawing. For isopropanes and α-X-isopropyl radicals, O^-, OH, NH_2 and F act as electron releasing, while NO_2 and CF_3 act as electron withdrawing. The strain energies of the cyclopropyl radicals (43.8–23.7 kcal/mol) are compared with those of similarly substituted cyclopropanes. Dipole moments and spin densities are reported.

There has been considerable theoretical [1–6] and experimental [7–10] interest in the effect of substituents on the structure of the cyclopropane ring. Ab initio molecular orbital calculations [11] show that π-acceptors result in a shortening of the distal bond and lengthening of the vicinal bonds, while the π-donors result in a shortening of the vicinal bonds and lengthening of the distal bond [12]. Cyclopropyl is more electronegative than 2-propyl; hence σ-donors stabilize the ring whereas σ-acceptors are destabilizing. Strong π-donors such as NH_2 and O^- are also able to stabilize cyclopropane [12].

The inversion barriers in α-monosubstituted methyl radicals are small or zero, with the largest barriers for substituents carrying a lone pair of electrons [13–15]. Increasing the substitution at the radical centre slightly increases the barriers to inversion, although from the experimental data, the methyl, and isopropyls appear to be planar [15–17], while the tertiary butyl radicals have a small barrier to inversion of about 0.5 kcal/mol [18, 19]. α-X-cyclopropyl radicals have larger inversion barriers than the alkyl radicals due to the ring strain. This is supported by experimental work on the α-chloro-cyclopropyl radical [20] and semiempirical calculations on the α-fluoro- and α-cyclopropyl radical [21]. The inversion of the cyclopropyl radical in solution [22, 23] and the α-methyl cyclopropyl radical [24] have been kinetically studied.

We study the effect of substituents (O^-, OH, NH_2, CH_3, NO_2, CHO, CN, F, and CF_3) on cyclopropane, α-cyclopropyl radicals, isopropane and α-isopropyl radicals using the semiempirical MINDO-Forces MO method [25].

We report the optimized geometries, heats of formation, electron densities, dipole moments, spin densities and strain energies.

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α-X-Cyclopropyl Radicals

Structural Details

As can be seen from the calculated heats of formation (Table 1), substituents with lone pairs cause deviations from planarity at the radical centre, and this is more pronounced in the case of NH_2 substituent, which is in agreement with ab initio calculations [2].

Table 1. Calculated heats of formation (ΔH_f, in kcal/mol) for α-X-substituted cyclopropanes, cyclopropyl radicals (planar and pyramidal), isopropanes, and isopropyl radicals (planar and pyramidal).

X	ΔH_f					
						
H	8.7	55.6	56.9	−25.8	7.4	8.2
O^-	5.6	−19.0	−16.0	− 1.7	−52.3	−51.4
OH	−39.1	− 5.7	− 4.4	−65.9	−49.0	−48.5
NH_2	11.6	31.3	30.8	−15.6	− 7.2	− 4.1
CH_3	6.9	36.3	40.3	−20.3	− 0.1	2.6
NO_2	− 0.7	24.7	32.4	−16.3	− 5.3	5.6
CHO	−23.4	7.8	13.9	−44.5	−24.9	−14.8
CN	29.9	63.3	66.8	6.3	26.9	27.5
F	−44.3	− 0.9	− 4.9	−82.5	−51.0	−51.0
CF_3	−178.9	−150.3	−149.3	−204.8	−187.7	−179.6

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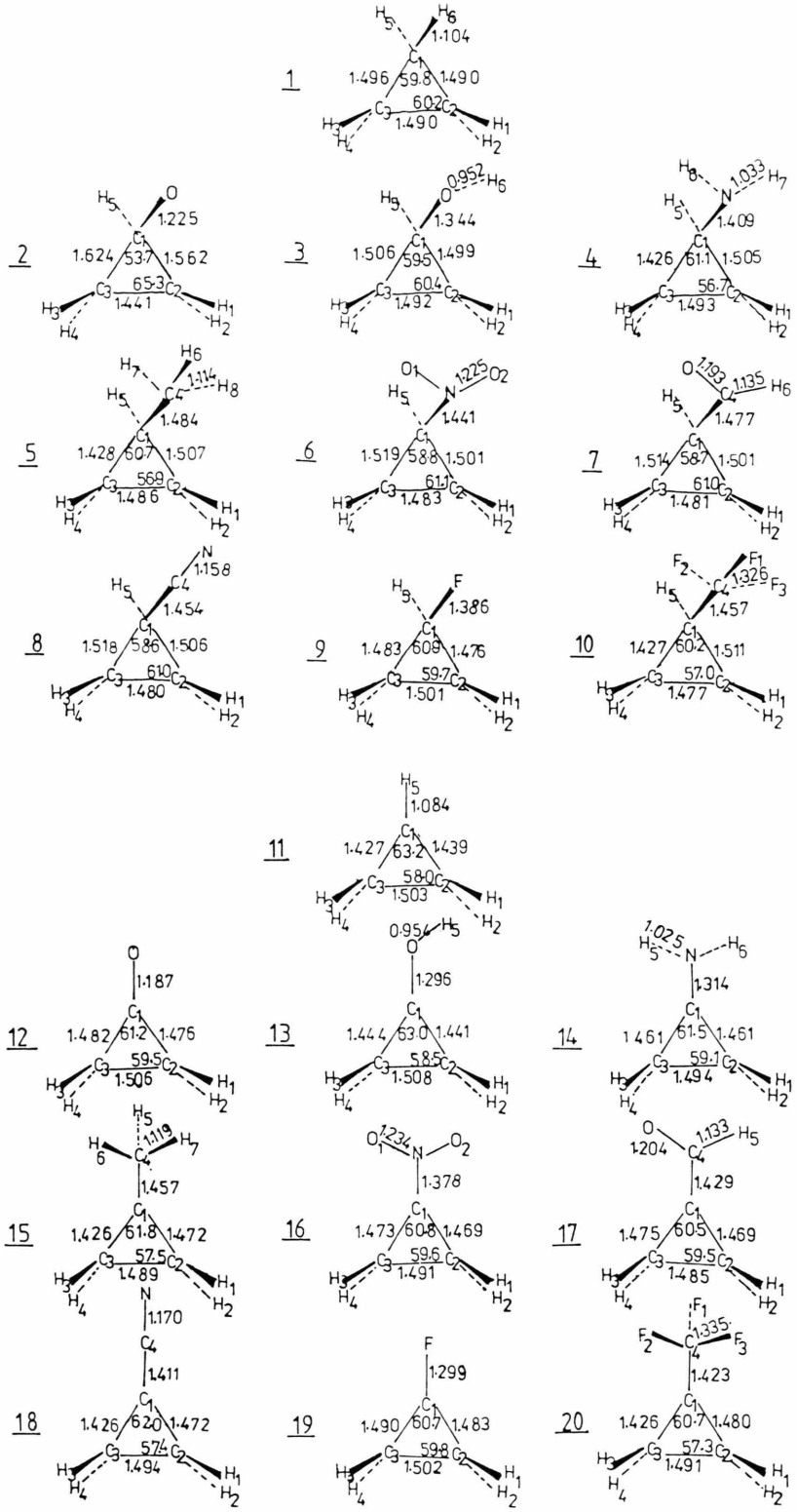


Figure 1. Structures of X-cyclopropanes (1 – 10) and cyclopropyl radicals (planar (11 – 20) and pyramidal (21 – 30)) as obtained from MINDO-forces calculations. Bond lengths are in Ångstroms and angles in degrees.

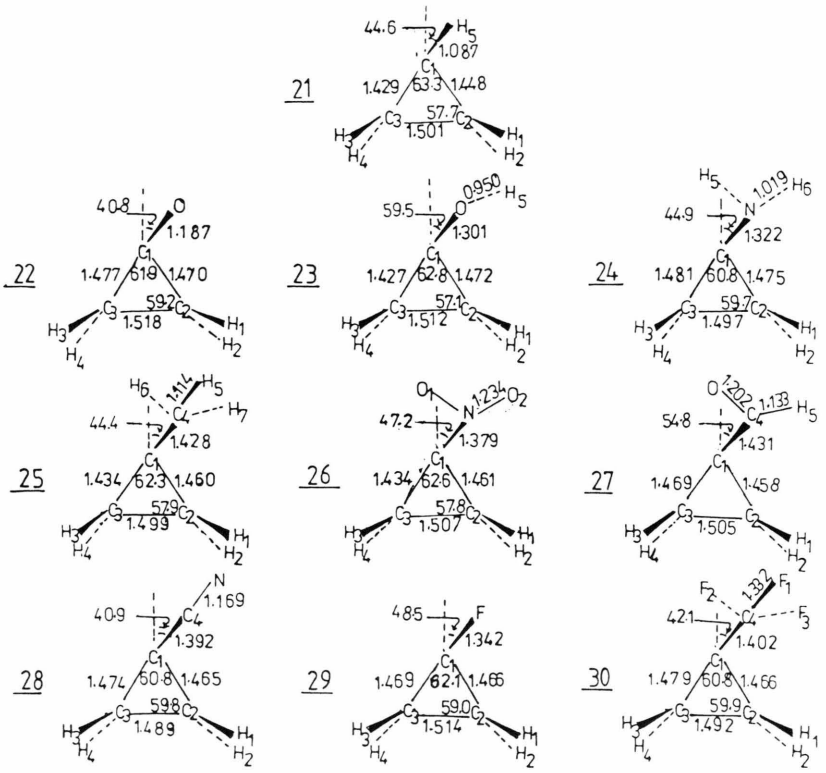


Figure 1. (continued).

F substituent shows also deviation from planarity, which is in agreement with semiempirical [21] and ab initio [2] calculations. There is sample experimental evidence that, as the electronegativity differences between the substituent and α-C increase, the radical becomes pyramidal [26]. An increase in the electronegativity of the α-substituent either causes [27–28] or parallels [29–31] an increase in bending at the radical center. This is in agreement with the present results for F substituent. Fluorine substituent does not act as π-donor, as originally assumed [32, 33], but predominantly as σ-acceptor. The geometries [34], reactivity [35] and destabilization [36] of fluoro-cyclopropanes can be explained on this basis.

The calculated out-of plan angle θ for α-X-substituted cyclopropyl radicals (Fig. 1) is in agreement with ab initio calculations [2]. The θ values from EPR [37] measurements on cyclopropyl radical ($\theta = 22.5°$) and α-methylcyclopropyl radical ($\theta = 22.9°$) are smaller than our values because the latter take no account of electron delocalization in the α-substituent and will therefore be underestimated. There are three other theoretical studies of cyclopropyl which also yield rather large θ values [38–40].

Comparison of the structure of the radicals with those for X-cyclopropanes shows that the generation of the radical by the abstraction of the hydrogen atom from cyclopropane results in a slight increase in the $C_3-C_1-C_2$ angles within the cyclopropyl ring (Fig. 1), which is in agreement with ab initio calculations [2].

In the pyramidal radicals the vicinal bonds are slightly longer, and distal bonds are slightly shorter except for the substituents O^-, OH, and F. Similar effects are obtained for the planar structures except for F substituent. It was found experimentally [41] that the vicinal bonds were decreased and the distal bond increased for cyclopropylamine, which is in agreement with the present calculations (Figure 1).

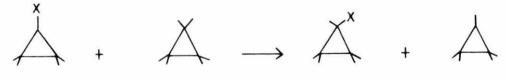
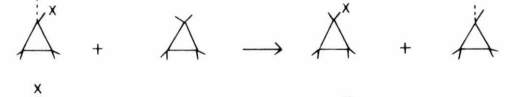
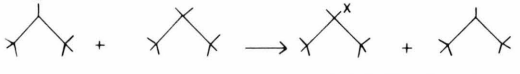
Electron Densities

It can be seen from Table 2, that the substituents F, O^-, and OH on the cyclopropanes decrease the electron densities on Cl and increase the electron densities on C2 and C3, i.e. act as electron releasing, while NH_2, CH_3, and CN act as a weakly electron releasing. For NO_2, CHO and CF_3 substituents, the electron densities increase on C1 and decreases on C2 and C3, i.e.

Table 2. Calculated electron densities of X-cyclopropanes and cyclopropyl radicals (planar and pyramidal). See Figure 1 for numbering.

Compd.	C1	C2	C3	C4	H1	H2	H3	H4	H5	H6	H7	H8	N	O1	O2	F1	F2	F3
1	3.983	3.979	3.983		1.011	1.011	1.008	1.008	1.009	1.008								
2	3.441	4.010	4.013		0.971	0.989	0.966	0.984	1.127					6.500				
3	3.647	4.017	4.062		0.991	1.003	0.988	1.000	1.082	0.757				6.453				
4	3.835	4.036	3.975		0.998	1.001	1.011	1.010	1.079	0.947	0.947		5.162					
5	3.950	4.019	3.959	3.919	1.003	1.003	1.022	1.010	1.028	1.026	1.032	1.028						
6	4.167	3.949	3.951		0.985	0.995	0.986	0.988	0.940				3.893	6.574	6.573			
7	4.099	3.947	3.975	3.377	1.004	1.004	1.004	0.997	0.977	1.145				6.470				
8	3.967	3.975	3.980	3.907	1.007	1.006	1.003	1.001	1.010				5.143					
9	3.563	4.051	4.050		0.972	0.998	0.969	0.996	1.052							7.350		
10	4.144	3.981	3.922	2.679	0.972	0.987	0.989	0.996	0.957							7.462	7.452	7.458
11	4.101	3.941	3.928		1.024	1.024	1.023	1.023	0.936									
12	3.420	4.121	4.117		0.973	0.973	0.971	0.971						6.452				
13	3.866	3.992	3.932		1.032	1.032	1.030	1.030	0.753					6.332				
14	4.098	3.930	3.928		1.043	1.035	1.040	1.034	0.953	0.954			4.985					
15	4.072	3.974	3.922	3.865	1.018	1.018	1.024	1.024	1.023	1.030	1.030							
16	4.150	3.987	3.927		0.986	0.986	0.984	0.984					3.895	6.581	6.581			
17	4.095	3.956	3.942	3.412	1.002	1.002	0.997	0.997	1.127					6.469				
18	4.041	3.974	3.924	3.875	1.009	1.009	1.015	1.015					5.137					
19	3.526	4.110	4.108		0.972	0.972	0.970	0.970								7.372		
20	4.186	3.950	3.881	2.679	0.989	0.989	0.995	0.995								7.436	7.449	7.449
21	4.081	3.947	3.938		1.026	1.008	1.027	1.006	0.967									
22	3.415	4.120	4.121		0.980	0.965	0.977	0.964						6.458				
23	3.882	3.994	4.004		1.008	1.007	1.016	1.008	0.756					6.384				
24	4.087	3.951	3.953		1.040	1.020	1.036	1.018	0.939	0.939			5.016					
25	4.068	3.957	3.941	3.867	1.025	1.010	1.032	1.007	1.033	1.027	1.033							
26	4.150	3.936	3.920		0.989	0.975	0.994	0.970					3.902	6.581	6.583			
27	4.160	3.936	3.952	3.403	1.007	0.992	1.012	0.989	1.134					6.468				
28	4.050	3.948	3.950	3.870	1.019	1.006	1.016	1.001					5.140					
29	3.643	4.046	4.043		0.983	0.998	0.981	0.986								7.329		
30	4.155	3.926	3.925	2.692	0.987	0.985	0.983	0.983								7.469	7.449	7.446

Table 3. Evaluation of substituent effects on cyclopropyl and isopropyl radicals.

	O^-	OH	NH_2	CH_3	NO_2	CHO	CN	F	CF_3
	71.6	13.5		17.6	21.5	15.7	13.6		18.4
			29.0					8.4	
	83.9	16.4	24.9	13.1	54.9	13.6	12.7	1.8	16.2

act as electron withdrawing. Similar results were found for the effect of substituents on pyramidal and planar cyclopropyl radicals, except for CHO on the planar radical, which acts as a weak electron releasing group.

Stabilization by Substituents

The stabilizing effect of a substituent is assessed by using an isodesmic reaction [42]. A positive heat of formation (Table 3) indicates stabilization of the reactant by the substituent. The results show that all the substituents are stabilizing; O^- substituent shows high stability, followed by NH_2, NO_2, and CF_3, while F shows low stability.

Dipole Moments

For the parent molecule, all substituents are found to increase the dipole moment (Table 4), especially NO_2 substituent. Same effect occurs on the cyclopropyl radicals and is found to be more pronounced for NO_2, CHO and CF_3 substituents.

Spin Densities

From Table 5 it can be seen that the unpaired electron density for the planar cyclopropyl radical lies mainly on C1 and is almost zero on C2 and C3 and partially on H1, H2, H3, and H4. For the pyramidal cyclopropyl radical, the electron density decreases on C1, increases on C2 and C3, and decreases on H1, H2, H3, and H4 compared with the planar cyclopropyl radical, and the spin density on H5 increases from 0.0 (planar) to 0.0169 (pyramidal). These results could be explained in terms of the interaction between Walsh orbital [43] and the unpaired electron orbital.

For the pyramidal cyclopropyl radical, the unpaired electron orbital lies out of the three-membered ring by an angle of 44.6°; this may cause a weak interaction between this orbital and the Walsh orbital, as seen from the spin electron density values in Table 5.

In the planar cyclopropyl radical the unpaired electron orbital tends to be perpendicular to the three-membered ring, which means that there is almost no interaction between this orbital and the Walsh orbital. This is supported by the obtained low spin electron density values on C2 and C3 in Table 5.

It was noticed from Table 5 that a substituent which has a lone pair electron such as NH_2 and OH, and high electronegativity, such as F, cause an increase in the electron densities on C2 and C3 for planar and pyramidal cyclopropyl radicals.

Table 4. Calculated dipole moments (in Debyes) of X-cyclopropanes, cyclopropyl radicals, isopropanes and isopropyl radicals.

	H	C^-	OH	NH_2	CH_3	NO_2	CHO	CN	F	CF_3
	0.013	3.890	1.845	1.429	0.093	4.042	3.219	2.576	1.993	3.350
	0.309	2.906	1.746	1.845	0.224	4.987	3.699	2.449	2.876	3.400
	0.671	2.996	1.672	1.603	0.397	4.918	3.622	2.448	2.435	3.447
	0.018	3.081	1.804	1.209	0.039	3.898	2.998	2.348	2.112	2.558
	0.008	3.338	1.767	1.444	0.026	4.779	3.515	2.453	1.928	2.910
	0.114	3.254	1.718	1.520	0.142	4.576	3.255	2.428	1.996	3.061

Table 5. Calculated spin densities of X-cyclopropyl radicals. See Figure 1 for numbering.

Compd.	C1	C2	C3	C4	H1	H2	H3	H4	H5	H6	H7	N	O1	O2	F1	F2	F3
11	0.774	0.000	0.000		0.055	0.055	0.056	0.056	0.000				0.116				
13	0.655	0.005	0.005		0.055	0.055	0.052	0.052	0.000								
14	0.528	0.021	0.020		0.045	0.030	0.046	0.029	0.029	0.028		0.219					
15	0.713	0.000	0.000	0.000	0.041	0.041	0.049	0.049	0.000	0.052	0.052						
16	0.637	0.001	0.001		0.034	0.034	0.032	0.032				0.049	0.088	0.089			
17	0.658	0.000	0.000	0.053	0.035	0.035	0.034	0.034	0.000				0.147				
18	0.648	0.000	0.000	0.002	0.035	0.035	0.043	0.043				0.190					
19	0.456	0.121	0.058		0.002	0.002	0.002	0.002							0.291		
20	0.690	0.000	0.000	0.033	0.034	0.034	0.043	0.043							0.006	0.057	0.057
21	0.722	0.057	0.050		0.057	0.034	0.042	0.036	0.016								
23	0.598	0.087	0.086		0.026	0.014	0.035	0.013	0.000				0.138				
24	0.512	0.058	0.059		0.032	0.013	0.031	0.012	0.000	0.001		0.277					
25	0.678	0.032	0.031	0.007	0.035	0.033	0.040	0.034	0.089	0.006	0.009						
26	0.581	0.052	0.050		0.022	0.027	0.026	0.028				0.050	0.079	0.080			
27	0.624	0.029	0.034	0.052	0.030	0.034	0.028	0.030	0.007				0.126				
28	0.632	0.021	0.022	0.009	0.033	0.029	0.031	0.026				0.193					
29	0.561	0.114	0.111		0.016	0.005	0.017	0.004							0.168		
30	0.613	0.030	0.032	0.067	0.027	0.025	0.024	0.023							0.134	0.010	0.010

α-X-Isopropyl Radicals

Structural Details

Experimental evidence suggests that the methyl, ethyl and isopropyl radicals are planar [15, 18, 19, 44]. At the UHF STO-3G level [2], the methyl radical is pyramidal with an out-of-plane angle of 15°, and substitution, particularly by substituents with lone pairs, increases θ [13–15, 44, 45]. At the RHF 3-21G//3-21G level [2], the isopropyl radical has $\theta = 23.1°$; this compares with UHF STO-3G value of 26.9° [15].

The present results (Table 1) show that the α-X-isopropyl radical prefers planar structure and that the stability is more pronounced in case of the cyano group. This is because the cyano group is a π-acceptor, and donation of the unpaired electron into the π^* orbital on cyano favors the planar structure [15, 45, 46].

The structure of the isopropyl radical differs from those of 2-propanes in which the C–X bond lengths are shorter in the radical (Fig. 2), which is in agreement with ab initio calculations [2].

Introduction of a substituent on isopropyl radical has little effect on C–C bond lengths and produces a small decrease in the C–C–C angle (Fig. 2) apart from the OH and F, which is similar to the 2-substituted allyl cations [47].

Electron Densities

Introduction of O^-, OH, NH_2 and F substituents on the 2-propanes causes a decrease in the electron densities on C2 and an increase on C1 and C3, i.e. act as electron releasing (Table 6). The CH_3 substituent shows weak electron releasing. NO_2 and CF_3 substituents cause an increase in the electron densities on C2 and a decrease on C1 and C3 i.e. act as electron withdrawing. The CHO substituent shows a weak electron withdrawing, while CN substituent shows no change on the three carbon atoms.

For the isopropyl radical, the effect of substituents is the same as in the case of 2-propanes apart from NH_2 and CN substituents. The NH_2 substituent acts as strongly electron releasing, and its power decreases on the pyramidal radical and shows no effect on planar isopropyl radical. The CN substituent shows no effect on the parent molecule and a slight increase in the electron releasing from the pyramidal to planar radicals.

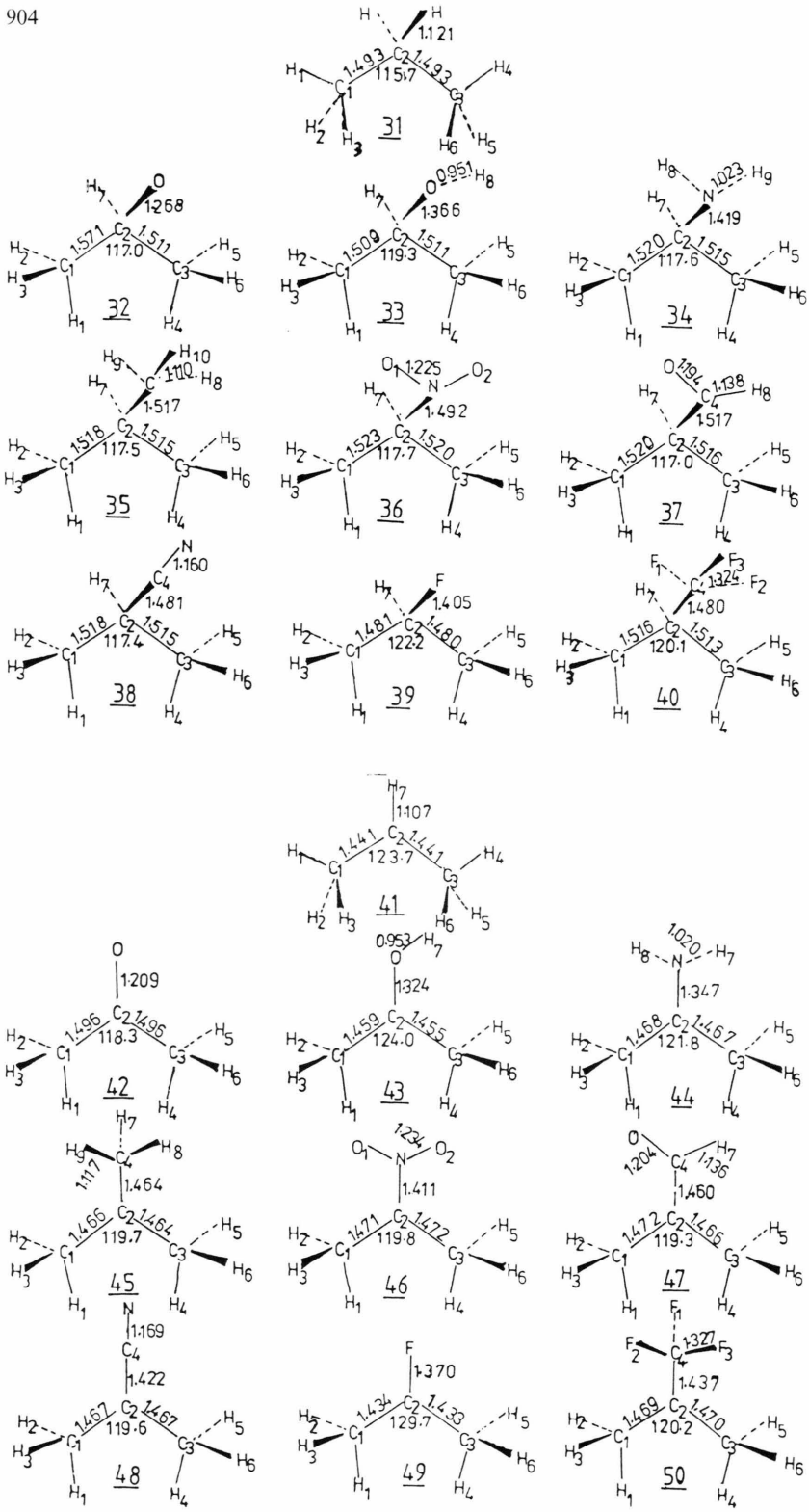


Figure 2. Calculated structures of X-isopropanes (31–40) and isopropyl radicals (planar (41–50) and pyramidal (51–60)). Bond lengths in Ångstroms and angles in degrees.

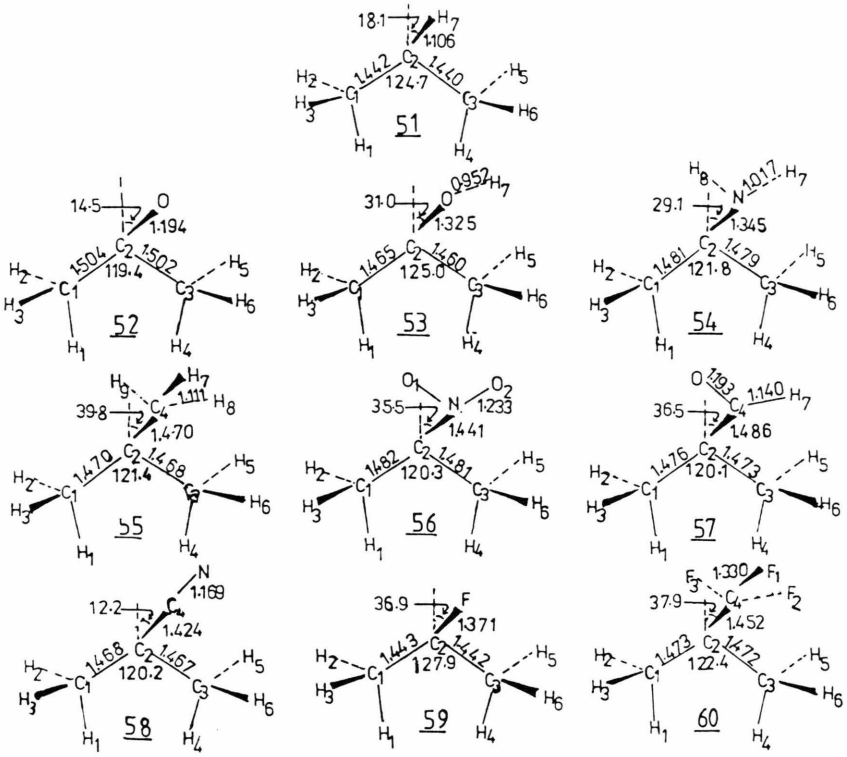


Figure 2. (continued).

Stabilization by Substituents

From Table 3, a positive heat of formation indicates stabilization of the reactant by the substituent. The results show that the substituents O^-, NO_2, and NH_2 are strongly stabilizing while F substituent is slightly stabilizing. This is inagreement with Dewar's argument [30] that the electronegativity of the substituent is not a factor which accounts for the increased configurational stability of the free radical. Electronegativity may be necessary but not sufficient to cause the radical to maintain it's configuration [48].

Dipole Moments

On the abstraction of a hydrogen atom from propane, the substituents O^-, OH, NO_2, CHO and CN cause an increase in the dipole moment from pyramidal to planar isopropyl radicals (Table 4), which may explain the high stability (Table 3) of O^- and NO_2. For NH_2, CH_3 and CF_3 substituents, there is an increase in the dipole moment for the pyramidal radical. For F substituent the dipole moment decreases from pyramidal to planar radicals, which may explains its low stability (Table 3).

Spin Densities

It can be seen from Table 7 that the electron spin densities for the unpaired electron lie mainly on C2, H2, H3, H5, and H6, while C1, H1, H4, and H7 have no electron spin densities because they lie in the plane of the planar radical.

For the planar radical, the substituent X is in the plane of the radical; thus the unpaired electron orbital is expected to be out of the plane of the radical. Therefore the interaction between this orbital and the hydrogen atoms H2, H3, H5, and H6 is expected to be larger than that of the atoms C1, C3, H1, H4, and H7, as can be seen from the electron spin densities in Table 7.

In case of a pyramidal radical it is expected that the singly occupied orbital interacts with all atoms, as can be seen from the electron spin densities.

It is noticed that CN substituent has a low spin density on H1, H4, and H7 because of the small angle ($\theta = 12.2°$) as compared with other substituents (Figure 2). But F substituent, which has $\theta = 36.9°$, has a high spin density on the corresponding atoms (H1, H4, H7).

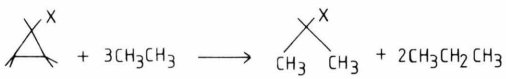
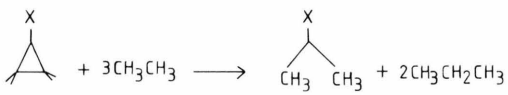
Table 6. Calculated electron densities of X-isopropanes and isopropyl radicals (planar and pyramidal). See Figure 2 for numbering.

Compd.	C1	C2	C3	C4	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	N	O1	O2	F1	F2	F3
31	3.943	3.909	3.933		1.024	1.026	1.025	1.022	1.026	1.026	1.037	1.038								
32	3.906	3.515	4.026		1.014	0.976	1.006	1.017	0.983	1.000	1.116					6.441				
33	3.984	3.589	4.013		1.021	0.988	1.013	1.016	1.003	1.011	1.120	0.759				6.483				
34	3.961	3.774	3.960		1.024	1.017	1.019	1.025	1.018	1.016	1.105	0.937	0.933		5.210					
35	3.937	3.916	3.938	3.935	1.025	1.030	1.021	1.028	1.027	1.019	1.044	1.025	1.026	1.028						
36	3.933	4.080	3.943		1.009	0.999	0.999	1.012	0.980	1.005	0.981				3.932	6.564	6.564			
37	3.922	4.033	3.933	3.402	1.023	1.014	1.012	1.019	1.023	1.013	1.002	1.140					6.463			
38	3.937	3.903	3.937	3.929	1.023	1.022	1.019	1.025	1.021	1.018	1.035				5.131					
39	4.005	3.517	4.008		1.018	0.965	1.011	1.018	0.967	1.008	1.084							7.400		
40	3.932	4.077	3.929	2.688	1.010	0.982	1.004	1.008	0.991	1.003	0.985							7.460	7.465	7.465
41	3.884	4.061	3.883		1.028	1.030	1.030	1.028	1.031	1.031	0.994									
42	4.068	3.437	4.067		1.011	0.976	0.976	1.011	0.975	0.975						6.503				
43	3.913	3.833	3.946		1.028	1.025	1.025	1.018	1.035	1.032	0.757					6.390				
44	3.881	4.063	3.879		1.030	1.045	1.049	1.029	1.047	1.048	0.942	0.941			5.045					
45	3.895	4.051	3.893	3.895	1.031	1.029	1.029	1.031	1.029	1.027	1.031	1.029	1.029							
46	3.908	4.120	3.905		1.012	0.982	0.982	1.011	0.984	0.983					3.935	6.589	6.590			
47	3.898	4.081	3.907	3.435	1.030	1.000	1.000	1.018	1.012	1.010	1.131					6.478				
48	3.899	4.021	2.898	3.904	1.028	1.021	1.021	1.028	1.020	1.020					5.139					
49	3.946	3.718	3.947		1.022	1.007	1.007	1.020	1.009	1.006								7.319		
50	3.896	4.154	3.887	2.690	1.015	0.991	0.991	1.019	0.992	0.991								7.462	7.455	7.455
51	3.884	4.058	3.885		1.033	1.030	1.026	1.034	1.029	1.025	0.997									
52	4.070	3.431	4.069		1.011	0.077	0.978	1.013	0.976	0.976						6.498				
53	3.916	3.824	3.947		1.031	1.017	1.027	1.024	1.031	1.027	0.758					6.397				
54	3.894	4.040	3.894		1.035	1.047	1.036	1.036	1.046	1.034	0.940	0.941			5.057					
55	3.895	4.046	3.897	3.896	1.031	1.036	1.022	1.034	1.033	1.020	1.032	1.029	1.028							
56	3.919	4.113	3.918		1.013	0.975	0.986	1.014	0.975	0.985					3.943	6.579	6.579			
57	3.903	4.089	3.907	3.420	1.028	0.996	1.005	1.021	1.015	1.006	1.141					6.469				
58	3.899	4.020	3.899	3.904	1.028	1.022	1.020	1.029	1.022	1.019					5.138					
59	3.965	3.684	3.964		1.030	0.985	1.007	1.030	0.985	1.004								7.347		
60	3.907	4.126	3.906	2.711	1.014	0.981	0.990	1.031	0.981	0.990								7.465	7.458	7.457

Table 7. Calculated spin densities of X-isopropyl radicals. See Figure 2 for numbering.

Compd.	C1	C2	C3	C4	H1	H2	H3	H4	H5	H6	H7	H8	H9	N	O1	O2	F1	F2	F3
41	0.000	0.761	0.000		0.000	0.059	0.059	0.000	0.059	0.059	0.000								
43	0.002	0.677	0.004		0.000	0.048	0.048	0.000	0.053	0.050	0.000				0.114				
44	0.005	0.581	0.005		0.001	0.037	0.039	0.001	0.039	0.039	0.012	0.012		0.223					
45	0.000	0.712	0.000	0.000	0.000	0.047	0.047	0.000	0.050	0.048	0.000	0.047	0.047						
46	0.003	0.631	0.003		0.000	0.042	0.043	0.000	0.043	0.042				0.044	0.072	0.071			
47	0.002	0.651	0.001	0.044	0.000	0.044	0.044	0.000	0.046	0.045	0.000				0.118				
48	0.000	0.652	0.000	0.001	0.000	0.043	0.042	0.000	0.043	0.043				0.171					
49	0.001	0.710	0.001		0.000	0.052	0.052	0.000	0.055	0.052							0.073		
50	0.002	0.688	0.001	0.030	0.000	0.044	0.044	0.000	0.045	0.030							0.004	0.046	0.047
51	0.000	0.755	0.000		0.002	0.051	0.064	0.004	0.053	0.064	0.000								
53	0.006	0.675	0.008		0.011	0.024	0.047	0.012	0.039	0.047	0.000				0.117				
54	0.023	0.545	0.024		0.017	0.028	0.021	0.017	0.029	0.020	0.009	0.009		0.252					
55	0.002	0.713	0.002	0.002	0.011	0.031	0.049	0.012	0.031	0.049	0.073	0.009	0.009						
56	0.009	0.664	0.176		0.010	0.031	0.039	0.011	0.021	0.039				0.046	0.064	0.061			
57	0.006	0.661	0.007	0.043	0.009	0.034	0.044	0.009	0.038	0.041	0.008				0.094				
58	0.000	0.653	0.000	0.002	0.001	0.041	0.043	0.001	0.041	0.043				0.169					
59	0.019	0.681	0.020		0.031	0.024	0.031	0.031	0.026	0.031							0.101		
60	0.012	0.656	0.012	0.045	0.014	0.028	0.036	0.014	0.029	0.036							0.099	0.006	0.006

Table 8. Calculated strain energies (kcal/mole) of X-cyclopropanes and cyclopropyl radicals.

	H	O^-	OH	NH_2	CH_3	NO_2	CHO	CN	F	CF_3
	−28.1	− 1.0	−20.4	−21.0	−20.9	− 9.2	−14.8	−17.2	−31.8	−19.5
	−41.8	−26.9	−36.9	−32.2	−30.0	−23.7	−26.3	−30.0	−43.8	−31.0

Strain Energies

The strain energy of α-X-cyclopropanes and α-X-cyclopropyl radicals can be estimated by comparing the strained energy with its free components using the group separation reaction from the equation 2, 3

$$+ 3CHCH \rightarrow CH_3ZCH_3 + 2CH_3CH_2CH_3, \quad (1)$$

where Z is CHX for α-X-cyclopropane and CX for α-X-cyclopropyl radicals.

In (1), two strained methylenes and a strained Z group are in the reactant, while the same groups, free from strain, are in the product. The exothermicity of this reaction, then, is a measure of the strain energy of the cylcopropane and cyclopropyl derivatives.

The strain energies of cyclopropanes and cyclopropyl radical derivatives are given in Table 8.

In Table 8, a comparison of the strain energies of the α-X-cyclopropyl radicals with those of the α-X-cyclopropanes shows that generation of the radical by abstraction of a hydrogen atom from cyclopropanes results in an increase in the strain energies within the cyclopropyl ring, which is in agreement with ab initio calculations [2].

Also it was found that F substituent shows a high strain energy compared with O^- substituent, which means that F substituent destabilizes the cyclopropyl radical, while O^- stabilizes the radical. This is in agreement with the values obtained from Table 3 for the effect substituents on the radicals.

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