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INTENSITIES OF IR BANDS OF CH STRETCHING VIBRATIONS AND ATOMIC CHARGES IN SATURATED THREE-MEMBERED RINGS

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The intensities of the absorption bands of the CH stretching vibrations in the IR spectra of solutions of cyclopropane, aziridine, oxirane, and thiirane in CCl_4 were measured. Quantum-mechanical calculations of these intensities were performed.

Attempts have been made in recent years to use data on the intensities of absorption bands in IR spectra to determine the charges on the atoms in molecules or organic compounds [1-7]. The fundamental possibility of obtaining information regarding the charges on the atoms from IR spectroscopic data is based on the modern interpretation of the behavior of vibrating molecules, which establishes a relationship (in analytical form) between the parameters of the electrooptical field and the characteristics of the distribution of the electron density on atoms or in bonds [1; 8, p. 155]. A limited number of charges on atoms found from the absolute intensities of the IR spectra (chiefly for simple hydrocarbons and halo-substituted methanes; for example, see [1]) are currently known. The charges on the atoms in the molecules of these compounds thus obtained are completely reasonable, and the data on the tendency of their change as a function of the type of chemical bond coincide with the data obtained by other methods. The complexity of distinguishing the individual bands in the IR spectra from the absolute intensities hinders the more extensive incorporation of the method of determining the charges based on a knowledge of the intensities. The intensities of the bands in the IR spectra the solutions of organic substances in inert solvents are of interest for expanding the possibilities of the use of IR spectroscopy in the study of the problem of the distribution of the electron density in molecules. The expedience of resorting to solutions is determined by the fact that nonvolatile compounds, for which recording of the IR spectra in the gaseous state is virtually impracticable, can be subjects of investigation in this case. In addition, the absence of resolution of the fine structure of the IR bands makes it possible to avoid the use of high pressures. As regards the effect of the solvent on the IR intensities, it is eliminated to a considerable extent if one is interested not in their absolute values but only in the course of the change in a certain series of compounds.

At the present time a great deal of data on the intensities of the bands of CH stretching vibrations (A_i) in the IR spectra of solutions of series of substituted methanes [9, 10], ethylenes [11], and acetylenes [12] has been accumulated. In interrelationship between the A_i^{soln} values found and the empirical characteristics of reactivity has been traced in order to ascertain general structural and spectrochemical principles [9-12]. Moreover, the question as to whether the actual charge distribution corresponds to the principles that are characteristic for the intensities of the IR spectra was not examined in [9-12].

In the present research the investigation of the intensities of the bands of the IR absorption spectra in the region of CH stretching vibrations was extended to solutions of saturated three-membered rings. The specific characteristics of these molecular systems are due to the ring strain peculiar to them and to the existence of interaction of the CH bonds with the ring heteroatom. The research pursues three interrelated goals:

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1. The elucidation of the degree to which the existing methods of quantum chemistry give a good approximation for the charges on the atoms in saturated rings both with respect to the absolute values and with respect to the tendencies of the change in them. To get around the principal difficulty of the quantum-chemical description of the pattern of distribution of the electron density – the dependence of the charge on the computational approximation selected – a set of charges on the atoms that is obtained for an approximation that ensures the greatest closeness of the calculated intensities of the IR spectra A_i^{calc} and their experimental values is considered to be best.

2. Testing of the approach in which the comparison of the trend in the change in the intensities of the IR spectra and the charges on the hydrogen atoms calculated quantum-chemically is regarded as a possible source of information regarding the changes in the real distribution of the electron density in the molecules.

3. An analysis of the reasons for the change in A_i as a function of the nature of the ring heteroatom and the ring strain.

The solution of these research problems required that we go beyond the bounds of three-membered rings [cyclopropane (I), aziridine (II), oxidrane (III), and thiirane (IV)] and to additionally study the acyclic compounds Me_2NH (V), Me_2O (VI), Me_2S (VII), H_2CO (VIII), MeCl (IX), MeF (X) $MeNO_2$ (XI), and $CHCl_3$ (XII).

The investigated I-IV were synthesized by means of known procedures; their physicochemical constants were in agreement with the literature data. Monomer VIII was prepared by depolymerization of paraformaldehyde by the method in [13]. The IR spectra of dilute solutions of I-IV and VIII in CCl_4 were recorded with an IKS-16 spectrometer. The conditions used for the methodical measurements of the intensities of the IR spectra were similar to those decribed in [9].

1. In the first stage of the research we calculated the A_i values for I-IV within the framework of variants of the Hartree–Fock–Roothaan (HFR) scheme: the semiempirical CNDO/2, MINDO/3, and MNDO variants and nonempirical variants in STO-3GF and 3-21GF bases. The theoretically calculated intensity of the i-th vibration $A_i^{calc} = (\pi N_A/3c)(\partial\mu/\partial Q_i)^2$ was compared with the corresponding experimental intensity measured either in the gaseous state or in solution in CCl (here, $\partial\mu/\partial Q_i$ is the derivative of the dipole moment of the molecule with respect to the i-th normal coordinate).

The optimized geometry of the molecules that we found in [14] was used in the nonempirical calculations in STO-3GF and 3-21GF bases and calculations by the MINDO/3 and MNDO methods. In the calculations by the CNDO/2 method we adopted a fixed geometry with the use of the Pople–Gordon "standard" geometrical parameters [15]. To calculate the derivatives of the dipole moments with respect to the vibrational symmetry coordinates $S_i(\partial\mu/\partial S_i)$ we varied the lengths of the CH bonds; in the nonempirical calculations the change in the length of the CH bonds was Δr_{CH} = ±0.005 Å, ±0.01 Å, as compared with Δr_{CH} = ±0.01 Å in the semiempirical calculations. In view of the high degree of distinctive character of the examined normal vibrations, the possibility of the existence of a complex form for them was disregarded and it was assumed that the squares of $\partial\mu/\partial S_i$ are proportional to the absorption intensities A_i. In the calculations we used CNDO, MINDO/3, MNDO, and GAUSSIAN-80 programs adapted for Soviet computers of the ES type.

The intergral intensities of the bands of the CH stretching vibrations of each type of symmetry were measured experimentally and calculated within various approximations (Table 1). According to the data in Table 1, the examined semiempirical methods, the most suitable for the calculation of the intensities of the IR spectra is the CNDO/2 method, which, as applied to all of the rings of I-IV, is capable of semiquantitatively reproducing the $A_i^{1/2}$ values (on averge with an accuracy of 5-10 $liter^{1/2} \cdot mole^{-1/2} \cdot cm^{-1}$). The MINDO/3 method substantially (by a factor of 1.5-3) elevates the $A_i^{1/2}$ values, while the MNDO method depresses them to approximately the same extent. Such a significant improvement in the results of the calculations on passing from the MNDO and MINDO methods to the CNDO/2 method does not seem unexpected, since it is evidently a characteristic peculiarity of the methods used (for example, see [17]. A shortcoming of the CNDO/2 method is the certain degree of instability of the results obtained by means of it. In addition to the satisfactory mean errors one observes substantial errors in the $A_i^{1/2}$ values for individual bands (particularly for the B_2 band in the IR spectrum of IV). The reasons for the existence of deviations for some bands and the absence for others are not clear.

TABLE 1. Square Roots of the Intensities of the Individual Bands of the IR Absorption Spectra in the Region of the CH Stretching Vibrations Calculated Quantum Mechanically and Determined Experimentally*

Compound	Type of symmetry	$A_{CH}^{1/2}$, liter$^{1/2}$ mole$^{-1/2}\cdot$cm^{-1}						Exptl.	
		semiempirical methods			nonempirical methods			gas [6, 16]	solution
		CNDO/2	MINDO/3	MNDO	STO-3GF	3-21GF	6-31GF**		
I	A_2	58	106	18	6	34	—	36,2	41,9
	E'_b	34	76	—	—	27	—	41,0	51,0
	E'_a	39	74	—					
II	A'	39	82	21	—	27		—	48,6
	A''	29				26			
	A'	38	—	—	—	22		—	38,2
	A''	23	—	—	—	21			
III	A_1	19	28	3	8	10	20,8	16,2	34,0
	B_1	29	73	5	—	18	46,3	43,9	—
	B_2	48	104	15	1	30	54,5	39,7	33,9
IV	A_1	20	40	—	—	28	—	—	29,0
	B_1	28	66	—	—	8	—	—	—
	B_2	39	90	—	—	1	—	—	11,3

*The frequencies of the CH stretching vibrations in the IR spectra of I-IV are not presented; they coincide with those published in [6, 14, 16].
**For comparison with the experimental values one should use the theoretically calculated total intensities of the two degenerate vibrations E' and E'_b and A' and A".

The use of the STO-3GF minimal basis for nomempirical calculations for I-III leads to $A_i^{1/2}$ values that are depressed by a factor of 2-15 as compared with the experimental values; this is in agreement with the data available in the literature. Thus, for example, in the case of the CH_3F molecule the difference in the intensities of the bands of the stretching vibations calculated in the STO-3GF basis and the experimentally measured values proves to be a tenfold difference [8]. The transition from the STO-GR basis to the 3-21GF basis improves the results appreciably. With the exception of two to three IR bands, the deviation between the $A_i^{1/2}$calc and $A_i^{1/2}$ values is in the range 210 liter$^{1/2}$-mole$^{-1/2}$-cm^{-1}. It is apparent that the nonempirical 3-21GF scheme also does not guarantee against marked deviations that substantially exceed the mean error (see the intensity of the band with A' symmetry in the IR spectrum of II). In the case of III one can see that even the use of the comparatively complete and flexible 6-31GF* basis does not ensure stable agreement between the calcualated $A_i^{1/2}$ values and the experimental values. It has been previously shown [19] in the case of several acyclic compounds (CH_4, C_2H_6, CH_3F, CH_3Cl) that calculations by the CNDO/2 method are more acceptable in the description of the intensities of the IR spectra of the band of the symmetrical CH vibration of the methyl group than nonempirical calculations of the "average" level of accuracy (4-31GF and 6-31GF bases), and we therefore decided to use this method in the second stage of this research.

2. According to the modern parametric theory of intensities of IR spectrra, the distribution of electron density between the atoms in molecules should also be characterized by the so-called quadratic effective charges χ_α and the equilibrium charges q^0_α, which are more widely used in chemistry [1]. The idea of the dominating role of equilibrium charges q^0_h in the changes in the total intensities of the IR bands is developed in [4]. Gussoni and coworkers [4] used the results of a study of the IR spectra of hydrocarbons with different hybridizations of the orbitals of the carbon atom as their basis. They found that the character of the change in q^0_h in a series of hydrocarbcons is symbatic to the change in the $\sum_i A_i^{\text{deform}}/\sum_i A_i^{\text{str}}$ ratio, where $\sum_i A_i^{\text{str}}$ and $\sum_i A_i^{\text{deform}}$ are the sum of the absolute intensities of the bands of stretching and deformation vibrations, respectively.

The selection of quadratic χ_H for comparison with the intensities of the IR spectra is justified, since, in contrast to equilibrium charges q^0_H then χ_H values take into account two important components: first, that part of the charge in the vibrating molecule which corresponds to the equilibrium positions of the shells of the atoms and, second, the part that depends on the deformation of the charge on the atoms in the case of vibrations around the equi-

librium positions. The χ_H values of a number of molecules with simple structures were previously determined from experiments through an expression that links the sum of all of the observed intensities $\sum_i A_i$ with the sum of the squares of χ_α over all α atoms [1].

These values, together with the mean intensities of all of the vibrational modes that change the lengths of the CH bonds ($\sum_i A_i/CH$), and the corresponding mean intensities of the bands of the CH vibrations in the IR spectra of solutions ($\sum_i A_i^{p-p}/CH$) are presented in Table 2. It is not difficult to convince oneself that the relationship between the mean absolute intensities $\sum_i A_i/CH$ and the squares of the effective charges on the hydrogen atoms χ_H^2 in the molecules of most compounds is expressed by a smooth curve. The regularity, which consists in the symbatic character of the change in $\sum_i A_i/CH$ and χ_H^2, is similar in general features to the behavior of the mean intensities of the bands of the CH stretching vibrations in the IR spectra of solutions $\sum_i A_i^{p-p}/CH$. This can probably be explained by the fact that the character of the redistribution of the electron density under the influence of structural factors play a much more important role in the formation of $\sum_i A_i^{p-p}/CH$ than the effect of the medium. The regularity found, despite its approximate character, may be useful for preliminary estimates of the effective charges on hydrogen atoms χ_H by means of interpolation of the data for investigated molecular systems with other charges.

The points of CH_3F, CHF_3, CH_2Br_2, and $CHBr_3$ deviate to the greatest extent from the smooth trend of the $\sum_i A_i/CH—q_H$ curves. (This is evidently a consequence of the fact that for them the ratio of the total intensities of the bands of the stretching vibrations and deformation vibations is substantially different than in the case of other compounds that are characterized by not too great inconstancy of the relative contributions of the stretching and deformation components.)

With the aim of evaluating the efficiency of quantum-chemical methods with respect to the behavior of quadratic effective charges we decided to compare the χ_H^2 values calculated by the CNDO/2 method with the mean intensities $\sum_i A_i^{p-p}/CH$ in the IR spectra of solutions of the investigated three-membered rings of I-IV and some compounds, the molecules of which do not have structural strain (formaldehyde, monosubstituted methanes, chloroform). The theoretical determination of χ_H^{calc} in this case reduced to calculations by the CNDO/2 method of the elements of the atomic polar tensors (APT), since the relationship between the invariant of the APT — the spur of the product of the matrixes $[P_H\tilde{P}_H]$ — and the charge χ_H^{calc} is described by the simple formula [2]

$$\chi^2_H = 1/3Sp[P_H\tilde{P}_H],$$

where P_H is an APT, which is a matrix of 3 × 3 order, as the elements of which the nine Cartesian components of the vector of the derivative of the dipole moment of the molecule with respect to the natural coordinate $\partial\vec{\mu}/\partial\tilde{r}_i$ serve.

The χ_H^{calc} values, presented in Table 2, were calculated by this method. Calculations by the CNDO/2 method generally lead to depressed χ_H^{calc} values as compared with the experimentally obtained χ_H values. A monotonic trend of the relationship between $\sum_i A_i^{p-p}/CH$ and $\chi^2{}_H{}^{calc}$ is not observed.

A much smaller volume of information regarding the effective charges was obtained by means of nonempirical quantum-chemical calculations [chiefly because the nonempirical self-consistent-field (SCF) methods prove to be too cumbersome for the indicated goal]. The available data are limited to molecules of III (χ_H = 0.087 unit) [6] and XII (χ_H = 0.082 unit) [25], for which the 6-31GF* and STO 4-GF bases used give a significant error in calculations of χ_H. Thus it may be concluded that the χ_H values on the whole are more sensitive to the selection of the computational approximation than the intensities of the IR spectra; the CNDO/2 method, which we selected as the working method, is not adequate in the description of the real distribution of charges in vibrating molecules. To this one must add that the q_H values found from IR spectroscopic experiments are reproduced far better within a relatively precise approximation (with the 6-31GF* basis and with allowance for the electron correlation) than in calculations in more economical "average" bases and in the semiempirical CNDO/2 method (see [3, 26]).

TABLE 2. Experimental and Calculated (by the CNDO/2 method) Effective Charges on the Hydrogen Atoms (χ_H) and "Mean" Intensities of the Bands of CH Stretching Vibrations in the IR Spectra ($\sum_i A_i$/CH)

Compound	χ_H, electron charge units (ecu)		$\sum_i A_i$/CH, mole^{-1}·liter·cm^{-2}		
	Exptl. [1, 20]	Calc.	solution [10]*	gas	literature source
I	0.10	0.10	725	499	[4]
II	—	0.11	955	—	—
III	0.12	0.11	570	942	[7]
IV	—	0.088	240	—	—
VI	—	0.10	600	—	—
VII	—	0.08	510	—	—
VIII	0.16	0.13	1800**	2780	[21]
IX	0.07	0.005	—	452	[22]
X	0.09	—	120	1230	[22]
XI	—	0.05	28	—	
XII	0.05	0.10	200	14	[23]
CHF_3	0.05	—	784	804	[23]
CH_2Cl_2	0.07	—	100	148	[23]
CH_2Br_2	0.12	—	143	67	[23]
$CHBr_3$	0.15	—	416	152	[23]
C_2H_4	0.10	—	—	417	[4]
t-BuC≡CH	0.20	—	3190***	3174	[24]

*The values obtained in the present research are presented for I-IV and VIII. The measurements were made with the participation of N. S. Kolodina.
**The mean intensity of two IR bands: 2915 cm^{-1} (A_1 = 2550) and 2845 cm^{-1} (A = 1050 mole^{-1}·liter·cm^{-2}).
***Data from [12].

3. Before we pass to the elucidation of the possibilities of the quantum-chemical approach for the study of the structural aspect of the intensities of the IR spectra, let us make one comment that touches upon the role of the ring heteroatom in the determination of $\sum_i A_i^{p-p}$/CH.

It is known that the regular decrease in the intensities of the IR absorption spectra in the region of CH stretching vibrations with an increase in the acceptor properties of substituent X is a general characteristic feature of molecules of the CH_3X and C_2H_3X types [10, 11]. On the other hand, as one can see from Table 2, $\sum_i A_i^{p-p}$/CH increases with the heteroatom in the rings of I-III is replaced in the order III < I < II, despite the order expected from the electronegativities of the C, N, and O atoms. The same anomaly was previously observed in the changes in $\sum_i A_i^{p-p}$/CH for V and VI, which are acyclic analogs of II and III. It is explained by the presence of an additional type of electron interaction: interaction between the unshared pair of electrons of the nitrogen or oxygen atom and the antibonding orbital of the trans-oriented CH bond [27]. In saturated rings the influence of the effect of the unshared pair of electrons should be considerably weaker than in their acyclic analogs, since the mutual orientation of the orbitals of the unshared pair of electrons and the CH bond in the ring cannot be characterized as a trans orientation "in pure form." As Gussoni and coworkers [4] assume, the greater observed A_i value for VIII as compared with III is explained precisely by this.

However, this reasoning does not apply to IV. It is known that the unshared pairs of sulfur atoms virtually do not participate in interaction with suitable (in symmetry) orbitals of CH bonds. To explain the observed decrease in $\sum_i A_i^{p-p}$/CH in the IR spectrum of IV as compared with $\sum_i A_i^{p-p}$/CH of the parent compound I one can use the concept of depletion of the CH parent compound I one can use the concept of depletion of the CH bond with respect to electron density of a molecule of IV as a consequence of its shift to the d orbitals of the sulfur atom (the d-orbital effect).

The spectral characteristics used in the research – the median intensities of the bands of stretching vibrations per CH bond and the intensities of individual bands of the IR spectra – were also drawn upon to discuss the problem of the source of reorganization of the electron density on passing from the investigated heterocycles in their acyclic analogs. According

TABLE 3. Physical Components ($\Delta\mu_{pc}/\Delta S_i$ and $\Delta\mu_{sp}/\Delta S_i$, D/Å) of the Derivatives of the Dipole Moment with Respect to the Symmetry Coordinates for Saturated Three-Membered Rings and Their Dimethyl Analogs*

Compound	Type of symmetry	Computational methods					
		CNDO/2		MNDO		3-21GF basis	
		$\Delta\mu_{pc}/\Delta S_i$	$\Delta\mu_{sp}/\Delta S_i$	$\Delta\mu_{pc}/\Delta S_i$	$\Delta\mu_{sp}/\Delta S_i$	$\Delta\mu_{pc}/\Delta S_i$	$\Delta\mu_{sp}/\Delta S_i$
I	A_2''	1,08	0.14	0.53	−1,53	1.12	−1.89
II	A'	−0,27	−0,21	0.27	−0,47	0.22	−0.74
	A''	0,98	0,13	0.62	−1,15	0.18	−0,67
III	A_1	−0,27	−0,16	0.14	−0,21	−0,05	−0,17
	B_2	1,85	−0,76	0.52	−1.22	0.21	−0.89
IV	A_1	0,34	0,11	—	—	1.05	−1,36
	B_1	—	—	—	—	0,99	−1.35
	B_2	1,72	0,82	—	—	1,38	−1,41
n·C_3H_8	B_2	—	—	0,76	1,04	0.89	0,36
V	A'	−0,27	−0,21	0.27	−0.47	−0,081	−1.70
	A''	0,98	0,13	1,32	1.06	−0,14	1,44
VI	A_1	−0,88	−0,38	—	—	−0.28	−0,79
	B_2	−1,15	−0,05	1.59	1.13	0,15	1,51
VII	A_1	0,63	0.23	—	—	1.02	−1,85
	B_1	0,35	0.08	—	—	1.15	−0,64
	B_2	0,78	0,30	—	—	1,52	−0,83

*To ensure comparability of the results with stretching corresponding to a predesignated form of vibration only four CH bonds in the molecules of the acyclic analogs (two from each methyl group) were treated.

to Table 2, the increase in $\sum_i A_i^{p-p}$/CH, that is due to elimination of the angular deformation upon opening of the ring is 30 (for the III and VI pair) or 270 mole^{-1}·liter·cm^{-2} (for the IV and VII pair). In order to ascertain the physical reason for the noted increase in $\sum_i A_i^{p-p}$/CH and the analogous increased in the individual intensities of the IR spectra we carried out the separation of the theoretically calculated derivatives of μ with respect to symmetry coordinates $\Delta\mu/\Delta S_i$ into components that have definite physical significance. According to [28], the derivative of the dipole moment with respect to the vibrational coordinate can be represented in the form of the sum of the "charge" (two terms) and "hybrid" components; the charge part is the set of point charges in the equilibrium and vibrationally excited states of the molecule multiplied by their radius vectors in the selected system of coordinates ($\Delta\mu_{т.з.}=\sum_A q^0{}_A\Delta r_A+\sum_A \Delta q_A r_A$) (A numbers the atoms of the molecule). "Hybrid" components $\Delta\mu_{sp}/\Delta S_i$ characterizes the intra-atomic sp polarization in the vibrational process:

$$\mu_{sp}=\sum_A p_{2s(A),\,2p_z(A)}\int \varphi_{2s(A)}\varphi_{2p_z(A)}\,d\tau,$$

where $p_{2s(A),\,2p_z(A)}$ is the order of the bond between the orbitals.

On the basis of the results of calculations of the derivatives of the dipole moments with respect to the symmetry coordinates (the latter are proportional to the intensities of the IR spectra $A_i^{\frac{1}{2}}$) we preferred the CNDO/2 method. In addition to that, we convinced ourselves that this method is of little use with respect to reproducing the experimentally found charges on the atoms χ_H and q_H^0. In this connection, for evaluating the contributions of the individual components to $\Delta\mu/\Delta S_i$, in addition to calculations by the CNDO/2 method, we made calculations by the MNDO method and nonempirical calculations in the 3-21GF basis, which made it possible to a great degree to form a judgment regarding the reliability of the results. The components of $\Delta\mu/\Delta S_i$ for the vibrations of different types of symmetry were calculated by three methods (Table 3). It is apparent that the CNDO/2 method diverges from the more precise semiempirical MNDO method and from ab initio calculations in the 3-21GF basis both with respect to the absolute values and with respect to the signs of the contributions to $\Delta\mu/\Delta S_i$. According to the CNDO/2 calculations the $\Delta\mu/\Delta S_i$ values are prefixed primarily by the contributions of the components of $\Delta\mu_{sp}/\Delta S_i$ are relatively small and change little with opening of the ring. On the other hand, according to the results of MNDO and ab initio calculations, the hybridization component makes the principal contribution to $\Delta\mu/\Delta S_i$ ($\Delta\mu_{sp}/\Delta S_i$

are greater by a factor of 2.5-3 than $\Delta\mu_{pc}/\Delta S_i$). It changes substantially on passing from the three-membered ring to the acyclic analog.

The material set forth above makes it possible to conclude that the intensities of the bands of the IR absorption spectra serve as a sensitive criterion of the changes in the hybridization state of vibrating CH bonds. The result that was obtained by the CNDO/2 method and attests to the fact that the supposedly leading contribution to the increase $\Delta A^{\frac{1}{2}}$ for the three-membered ring as compared with the contribution for the dimethyl derivative is due to the "charge" component is, in our opinion, a reflection of the inadequacies of the method. To be more precise, it is a consequence of the incorrect allowance for, in the CNDO/2 method, the integrals of electron repulsion with the s and p functions of one or two adjacent atoms. According to the CNDO/2 computational scheme these integrals are not individualized but are averaged to unit integrals γ_A and γ_{AB}.

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