of sulfur which makes the dipolar structure $R_2N\cdot^+\text{-}X^-$ more disfavored, relative to the $R_2N\text{-}X\cdot$ structure, for $R_2NS\cdot$ than for $R_2N\dot{O}$. The same factors dominate the EPR spectrum we have assigned to diphenyliminothiyl, $Ph_2C{=}N\dot{S}$. That is, the g factor for this radical is much larger than that found for iminoxy radicals (i.e., 2.015 vs. ~2.005) while the nitrogen splitting is smaller (i.e., 18 vs. ~32 G).

From a chemical point of view, $R_2NS\cdot$ radicals are virtually unique. They couple at (or near) the diffusion-controlled limit but are extremely unreactive toward many molecular substrates that react readily with a majority of free radicals. In this latter aspect, their behavior is analogous to that of nitroxides. However, in their ready head-to-head dimerization, the behavior of aminothiyl radicals differs from nitroxides since only relatively unhindered nitroxides couple reversibly,[5,16,17] and this coupling probably involves a four-center dipole–dipole bond rather than an O to O coupling. The bond strengths in the nitroxide dimers ($\Delta H \leq 8$ kcal/mol)[17] are less than one-third as large as the bond strengths in the aminothiyl radical dimers (ca. 27 kcal/mol). These differences can be attributed to the greater strength of S-S bonds compared with O-O bonds. Our failure to cleave the S-S bond of bis(diphenyliminyl) disulfide by heating can also be accounted for on bond strength grounds since, in the case of the oxygen analogues, it is known that iminoxy radicals form stronger O-R′ bonds than do nitroxides.[18]

Our results confirm Bennett et al.'s conclusion that bis(dialkylamino) disulfides can be reversibly decomposed by heating to yield dialkylaminothiyl radicals. The S-S bond strength is ca. 27 kcal/mol, and this bond can be cleaved by uv photolysis in solution. However, in solid matrices, photolysis leads to at least some N-S bond cleavage.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XXIII. Cyanomethyl Radicals[1]

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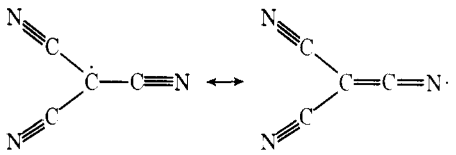
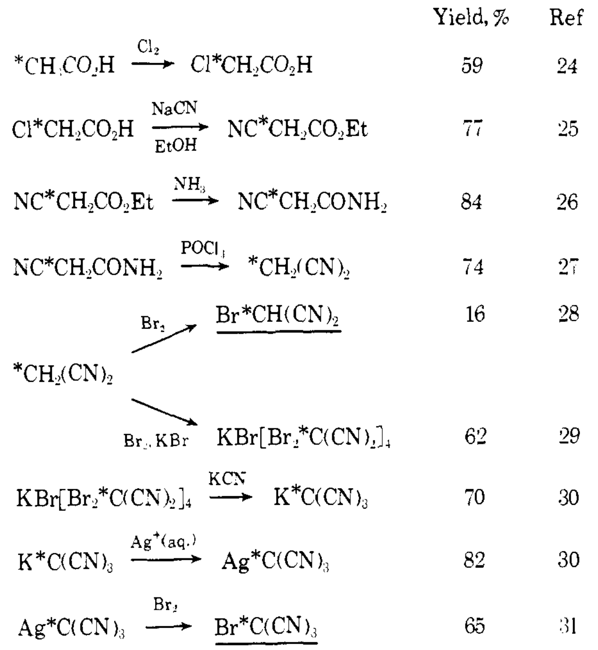
Abstract: Dicyanomethyl and tricyanomethyl have been prepared and examined by EPR spectroscopy. Their EPR parameters at 20° are: $H\dot{C}(CN)_2$, $g = 2.0033$, $a^{H} = 19.18$, $a^{N} = 2.75$, $a^{^{13}C_\alpha} = 29.18$ G; $\dot{C}(CN)_3$, $g = 2.0033$, $a^{N} = 2.28$, $a^{^{13}C_\alpha} = 22.06$, $a^{^{13}C_\beta} = 18.20$. It is concluded, on the basis of the $^{13}C_\alpha$ couplings and from the results of INDO calculations, that both radicals are planar. The $^{13}C_\alpha$ couplings, which were measured with enriched material, increase slightly with increasing temperature because the magnitude of the out-of-plane vibrations of the C_α substituents increases. Both radicals decay with second-order kinetics, the $H\dot{C}(CN)_2$ radical at close to the diffusion-controlled limit ($k^2{}_{EPR} = 1.2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at 20°), but $\dot{C}(CN)_3$ decays considerably more slowly.

It has been conclusively demonstrated that the majority of long-lived carbon-centered radicals owe their persistence *primarily* to steric effects.[3] Radicals of the triphenylmethyl type are probably no exception,[3] but with such radicals it is difficult to separate the steric influence of the three aromatic rings from the effect they have by virtue of their ability to delocalize the unpaired electron. For this reason, we decided to investigate the kinetic behavior of a carbon radical which, though similar to triphenylmethyl in having three adjacent π-bond systems capable of delocalizing the unpaired electron, had only minimal steric protection of the radical center. As our radical we chose tricyanomethyl, $\dot{C}(CN)_3$, which should be long-lived *if* p-π delocalization does indeed contribute significantly to persistence. Because of this delocalization, tricyanomethyl is expected to be planar. However, with three highly electronegative groups it was not utterly inconceivable that $\dot{C}(CN)_3$ would be nonplanar (like $\dot{C}F_3$[4] and $\dot{C}Cl_3$[5]). This makes its EPR spectroscopy particularly interesting.



Tricyanomethyl has not been reported, but there have

Scheme I



	Yield, %	Ref
$^{*}CH_3CO_2H \xrightarrow{Cl_2} Cl^{*}CH_2CO_2H$	59	24
$Cl^{*}CH_2CO_2H \xrightarrow[EtOH]{NaCN} NC^{*}CH_2CO_2Et$	77	25
$NC^{*}CH_2CO_2Et \xrightarrow{NH_3} NC^{*}CH_2CONH_2$	84	26
$NC^{*}CH_2CONH_2 \xrightarrow{POCl_3} {}^{*}CH_2(CN)_2$	74	27
$^{*}CH_2(CN)_2 \xrightarrow{Br_2} \underline{Br^{*}CH(CN)_2}$	16	28
$^{*}CH_2(CN)_2 \xrightarrow{Br_2, KBr} KBr[Br_2{}^{*}C(CN)_2]_4$	62	29
$KBr[Br_2{}^{*}C(CN)_2]_4 \xrightarrow{KCN} K^{*}C(CN)_3$	70	30
$K^{*}C(CN)_3 \xrightarrow{Ag^{+}(aq.)} Ag^{*}C(CN)_3$	82	30
$Ag^{*}C(CN)_3 \xrightarrow{Br_2} \underline{Br^{*}C(CN)_3}$	65	31

been many EPR studies of other aliphatic nitrile radicals in solution.[6-21] The simplest cyanomethyl, $H_2\dot{C}CN$, has been investigated in detail,[8,13,15,19,21] but only preliminary reports on dicyanomethyl, $H\dot{C}(CN)_2$, have appeared.[19,21] In this paper we compare the solution EPR parameters of $\dot{C}(CN)_3$, $H\dot{C}(CN)_2$, and $H_2\dot{C}CN$, and describe studies of the decay kinetics of the first two of these radicals.

Experimental Section

The general experimental procedures and kinetic EPR technique have been described previously.[22]

The *dicyanomethyl* radical was generated in two ways: first, by photolysis of a saturated solution of malononitrile in 1:1 (v/v) benzene-di-*tert*-butyl peroxide (substitution of toluene or isopentane for the benzene gave the EPR spectra of radicals derived from these hydrocarbons); second, by photolysis of ca. 0.1 g of bromomalononitrile dissolved in a mixture of di-*tert*-butyl peroxide (0.15 ml), trichlorosilane (0.10 ml), and toluene (0.15 ml). The second method gave the better spectrum of $H\dot{C}(CN)_2$ and allowed measurements to be made over a greater range of temperatures. The first method gave a less satisfactory spectrum, and, on prolonged photolysis (ca. 1 hr), a persistent radical ($\tau_{1/2} \sim$ hours) having just *three* equivalent nitrogens ($a^N \sim 1.6$ G) was sometimes obtained. This radical, which was never produced in the bromomalononitrile system, was not identified.

Attempts were made to generate the *tricyanomethyl* radical by a variety of photolytic and nonphotolytic routes, but only two methods were at all successful. Reasonable EPR spectra of $\dot{C}(CN)_3$ were obtained by photolysis of bromotricyanomethane (ca. 0.05 g) in a mixture of di-*tert*-butyl peroxide (0.15 ml), toluene (0.15 ml), and either tri-*n*-butylsilane (0.03 ml) or trichlorosilane (0.03 ml). The former method was less satisfactory. The EPR spectra were weaker, and a reddish-orange solid[23] was precipitated immediately unless the sample was made up at temperatures below −30°. This solid was formed rapidly upon photolysis of these samples at any temperature. Fortunately, the trichlorosilane system gave a homogeneous reaction mixture even when made up at room temperature, and, during the first 1 or 2 min of photolysis, this system gave such intense EPR spectra of $\dot{C}(CN)_3$ that the β-^{13}C and even the α-^{13}C hyperfine splittings (hfs) could be measured from the ^{13}C present in natural abundance. However, after 2 or 3 min of photolysis, the reddish orange solid was again formed and the intensity of the $\dot{C}(CN)_3$ signal decreased markedly. Each measurement of the rate constant for $\dot{C}(CN)_3$ decay therefore required a fresh sample and each sample could only be photolyzed for 1-2 min. The decay rate constants could not be determined with our usual accuracy, particularly at temperatures above 0° where the solid was formed more rapidly than at lower temperatures.

Table I. EPR Parameters for Cyanomethyl Radicals[a]

Radical	Temp, °C	g	a^H	a^N	$a^{^{13}C\alpha}$	$a^{^{13}C\beta}$
$H_2\dot{C}CN$[b]	33	2.00296	21.00	3.50		
$H\dot{C}(CN)_2$	20	2.0033	19.18	2.75	29.18[c]	
$\dot{C}(CN)_3$	20	2.0033		2.28	22.06[c]	18.20

[a] Hyperfine splittings are given in gauss. [b] Data from ref 13. [c] From ^{13}C-enriched material.

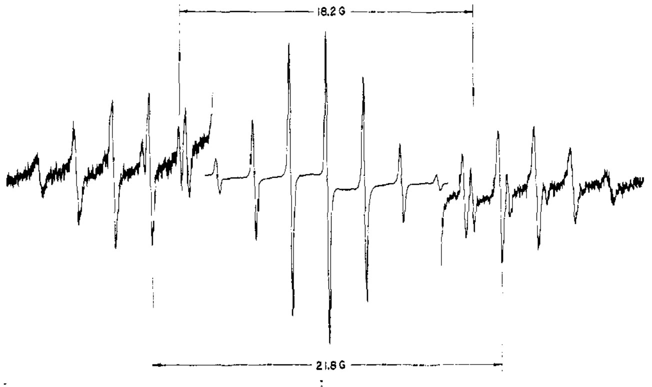


Figure 1. EPR spectrum of $\cdot C(CN)_3$ taken at −36° with the di-*tert*-butyl peroxide-trichlorosilane system using bromotricyanomethane-*1*-^{13}C (18.2 atom % ^{13}C). The outer portions of the spectrum were recorded at a gain ten times that of the central septet. The β-^{13}C hfs is 18.2 G and the α-^{13}C is 21.8 G.

In order to study the EPR spectroscopic properties of $H\dot{C}(CN)_2$ and $\dot{C}(CN)_3$ in greater detail, the corresponding bromides were prepared with ^{13}C enrichment at the α-carbon. The procedure which is outlined in Scheme I, involved known literature methods[24-31] starting from acetic acid-*1*-^{13}C (Merck, Sharp and Dohme, Canada, Ltd.). Bromomalononitrile-*1*-^{13}C (27.4 atom % ^{13}C by mass spectrometry) was prepared in an overall yield of 4.5% and bromotricyanomethane-*1*-^{13}C (18.2 atom % ^{13}C by mass spectrometry) in 6.5% overall yield.

Normal bromomalononitrile and bromotricyanomethane were prepared via the same route as the labeled compounds except that malononitrile (Eastman, practical grade) was the starting material in both cases.

Bromomalonitrile: mp 61-65° (lit.[28] 63-64°); proton NMR (CCl_4) τ 5.10, ($CDCl_3$) 4.94.

Bromotricyanomethane: mp 74-76° dec, sealed tube (lit.[31] 72° dec).

Results

EPR Spectra. The hyperfine splittings and g values for the three cyanomethyl radicals are given in Table I. For the $H\dot{C}(CN)_2$ radical, a^H and a^N were independent of the temperature (−60 to 20°), but $a^{^{13}C_\alpha}$ increased slightly as the temperature was raised. Its temperature dependence could be described by

$$a^{^{13}C_\alpha}[H\dot{C}(CN)_2] = (29.12 \pm 0.02) + [(4.45 \pm 0.44) \times 10^{-3}]t, \text{G}$$

where t is in °C.

The EPR spectrum of $\dot{C}(CN)_3$ is shown in Figure 1. It consists principally of a simple septet (1:3:6:7:6:3:1) arising from the three equivalent nitrogens, together with the satellite lines due to the α- and β-^{13}C. Within experimental error, a^N was temperature independent, but $a^{^{13}C_\alpha}$ again increased with increasing temperature:

$$a^{^{13}C_\alpha}[\dot{C}(CN)_3] = (21.98 \pm 0.01) + [(4.92 \pm 0.36) \times 10^{-3}]t, \text{G}$$

The temperature dependence of $a^{^{13}C_\beta}$ was not investigated since the β-^{13}C satellite lines were not sufficiently intense at natural abundance.

INDO Molecular Orbital Calculations. The three cyanomethyl radicals were studied by INDO calculations using standard procedures.[32,33] That is, all bond lengths and angles, except the $N^{\beta}C^{\alpha}C$ angle which was taken to be 180°, were varied in order to find the geometry that yielded the lowest total energy for each radical. The equilibrium geometries (which are appended to Table II) indicated that all three radicals are planar. The procedures for $H_2\dot{C}CN$ and $H\dot{C}(CN)_2$ were quite straightforward, but there were convergence problems near the equilibrium geometry with $\dot{C}(CN)_3$. However, these problems were overcome by using as the starting point a geometry where the program did converge (r_{CC} = 1.40 Å, r_{CN} = 1.15 Å). The SCF orbitals of this geometry were then used as the initial estimate for the orbitals of the new geometry (obtained by changing a bond length by a small increment). This process (i.e., the orbitals of the previous geometry serving as the starting point for the next geometry) was repeated until the equilibrium geometry was obtained. The π-spin densities (ρ^{π}) and hyperfine splittings obtained by these calculations are given in Table II.

Radical Decay Kinetics. The dicyanomethyl radical, produced by photolysis of a di-*tert*-butyl peroxide, benzene solution of malononitrile, decayed with "clean" second-order kinetics.

$$2H\dot{C}(CN)_2 \xrightarrow{k^2_{EPR}} \text{products}$$

At room temperature and with initial radical concentrations in the range 1-3 × 10^{-7} *M*, the decay rate constant, k^2_{EPR}, was found to be 1.2 × 10^9 M^{-1} sec^{-1} which is equal to (or close to) the diffusion-controlled limit.

The tricyanomethyl radical, produced from $BrC(CN)_3$ and $SiCl_3$, also decayed with "clean" second-order kinetics at temperatures from −60 to 20° and with initial radical concentrations in the range 10^{-5} to 10^{-6} *M*. The measured rate constants for decay, which are given in Table III, indicate that this reaction occurs at a rate significantly below the diffusion-controlled limit and also serve to illustrate the scatter of our experimental data for this radical. These inaccuracies arose because formation of the reddish orange solid severely limited the duration of each experiment (see above). The "slow" decay of $\dot{C}(CN)_3$ is probably due to a small activation energy for the combination of these radicals. Unfortunately, the formation of the solid prevented us from discovering whether decay occurred mainly by a head-to-head

$$2\dot{C}(CN)_3 \rightarrow (CN)_3CC(CN)_3$$

or a head-to-tail reaction[34]

$$2\dot{C}(CN)_3 \rightarrow (CN)_2C{=}C{=}NC(CN)_3$$

Table II. Selected Results of INDO Calculations on Cyanomethyl Radicals with Optimized Geometries[a]

	$H_2\dot{C}CN$[b]	$H\dot{C}(CN)_2$[c]	$\dot{C}(CN)_3$[d]
ρ_N^{π}	0.6057	0.4325	0.3619
$\rho_{C_\alpha}^{\pi}$	0.6509	0.5797	0.5058
$\rho_{C_\beta}^{\pi}$	−0.2567	−0.2223	−0.1972
a^H	−20.7	−20.9	
a^N	6.2	4.5	3.8
$a^{^{13}C\alpha}$	29.8	25.0	19.8
$a^{^{13}C\beta}$	−21.7	−19.1	−17.5

[a] Hyperfine splittings in gauss. [b] Calculated for a planar radical with r_{CC} = 1.35 Å, r_{CN} = 1.23 Å, r_{CH} = 1.11 Å, $\beta C\alpha CH$ angle = 123°. [c] Calculated for a planar radical with r_{CC} = 1.38 Å, r_{CN} = 1.21 Å, r_{CH} = 1.12 Å, $\beta C\alpha CH$ angle = 121°. [d] Calculated for a planar radical with r_{CC} = 1.39 Å, r_{CN} = 1.21 Å, $\beta C\alpha C\beta C$ angle = 120°.

Table III. Rate Constants (M^{-1} sec^{-1}) for Decay of $\dot{C}(CN)_3$ Radicals

Temp, °C	$k^2_{EPR} \times 10^{-6}$	Temp, °C	$k^2_{EPR} \times 10^{-6}$
22	4.8	−40	2.6
0	5.2	−40	2.6
−10	8.9	−50	4.0
−20	5.4	−60	4.2
−20	6.4	−60	1.0
−30	2.9		

Discussion

As a consequence of the increasing extent of electron delocalization, a planar radical conformation will be increasingly favored along the series $\dot{C}H_3$, $H_2\dot{C}CN$, $H\dot{C}(CN)_2$, and $\dot{C}(CN)_3$. Since methyl is planar, or close to it,[35,36] the three cyanomethyl radicals should also be planar. This conclusion receives support from the experimental values of $a^{^{13}C_\alpha}$ and from the INDO calculations. Thus, since $a^{^{13}C_\alpha}$ is 38.3 G for methyl,[37] the $H\dot{C}(CN)_2$ (29.2 G) and $\dot{C}(CN)_3$ (22.1 G) radicals must be at least as near to planar as methyl. The reliability of the INDO calculations is indicated both by the satisfactory agreement between calculated (Table II) and measured (Table I) hyperfine coupling constants, and by the fact that the calculated and measured couplings (except for a^H) show the same trends.

The sensitivity of $a^{^{13}C_\alpha}$ to small deviations of a radical from a planar geometry means that this coupling is usually dependent on the temperature. This dependence arises because, for a planar radical, the magnitude of the out-of-plane vibrations of the C_α substituents increases with the temperature. The measured temperature coefficients of $a^{^{13}C_\alpha}$ for $H\dot{C}(CN)_2$ and $\dot{C}(CN)_3$ were ca. 4.5 and 4.9 mG/deg, respectively, which may be compared with 22 mG/deg for $H_2\dot{C}OH$[38] and ca. 5 mG/deg for tris(3,5-di-*tert*-butylphenyl)methyl[39] over similar ranges of temperature. The cyanomethyl and triphenylmethyl types of radicals are "stiffened" by electron delocalization since this gives the C_α-C_β bonds some double-bond character. Out-of-plane vibrations are therefore reduced, and the $a^{^{13}C_\alpha}$ temperature coefficients are smaller than for localized radicals such as $H_2\dot{C}OH$.

The values of $a^{^{13}C_\alpha}$ and $\rho_{C_\alpha}^{\pi}$ for $\dot{C}(CN)_3$ (22.1 G and 0.51) are similar to the values found for tris(3,5-di-*tert*-butylphenyl)methyl (23.6 G at 25° and 0.48 or 0.52),[39] which implies that the unpaired electron is delocalized to approximately the same extent in both radicals. The increase in $a^{^{13}C_\alpha}$ with temperature for the latter radical was suggested[39] to be partly due to a small increase in twisting of the phenyl rings (which would give a slightly enhanced spin density at C_α because electron delocalization would be decreased). However, the similarity in the $a^{^{13}C_\alpha}$ temperature coefficients for these two radicals suggests that any contribution from phenyl twisting is of less importance than the contribution from out-of-plane bending (since the CN groups in $\dot{C}(CN)_3$ cannot twist out of conjugation).

The bimolecular self-reaction of $H\dot{C}(CN)_2$ radicals occurs at, or close to, the diffusion-controlled limit, as we would expect since electron delocalization normally appears to have little effect on the rates of such processes.[3] The relatively slow decay of $\dot{C}(CN)_3$ radicals was therefore somewhat surprising to us. Since it seems unlikely that the retardation of the $\dot{C}(CN)_3$ radical combination could be produced by steric or polar[40] effects, it must be attributed to electron delocalization. We suggest that a small activation energy for this combination is required because, in attaining the transition state for reaction, one or both radicals must be distorted from a strongly preferred planar geometry. However, the small magnitude of the energy barrier to combination in a radical in which the spin density at the α carbon is about as low as that in triphenylmethyl[39] serves to confirm our view[3] that radical lifetimes generally depend very much more on steric than on electronic factors.

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(40) In the gas phase, the rate constants for the combination of $\cdot CH_3$ and of $\cdot CF_3$ radicals are virtually equal; see, e.g., J. A. Kerr in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 1.

Analysis of the Reactivity of Alkenylidenecyclopropanes in Cycloaddition Reactions

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Abstract: The second-order rate constants for the cycloaddition reactions of substituted alkenylidenecyclopropanes with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in dichloromethane have been measured and found to fall in the range of ~2 to ~40 M^{-1} sec^{-1}. The reaction of 2-phenylisobutenylidenecyclopropane with PTAD is characterized by $\Delta H^\ddagger = 9.6 \pm 1.5$ kcal/mol and $\Delta S^\ddagger = -23 \pm 3$ eu. Methyl groups attached to the three-membered ring increase the reactivity of the alkenylidenecyclopropanes, while unsaturated groups, such as phenyl and ethynyl, lead to reductions in reactivity. In the unsymmetrically substituted 2,2-dimethyl- and 2,2,3-trimethylisobutenylidenecyclopropane, the dominant mode of attack by PTAD occurs at the most highly methylated ring carbon atoms. The reactivity and mode of reaction of the substituted alkenylidenecyclopropanes with PTAD is discussed in terms of the ionization potentials of the HOMO's and the results of CNDO calculations and frontier molecular orbital theory. The detailed analysis of the cycloaddition reaction leads to the conclusion that the cycloaddition is concerted and occurs via a very early transition state which is orbitally controlled.

Recent investigations in our laboratories of cycloaddition reactions of cyclopropane-containing compounds have revealed rather dramatic differences in reactivity and mode of reaction. Whereas alkenylidenecyclopropanes (**1**) react rapidly with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to produce adducts of general structure **3**,[2] methylenecyclopropanes[3] and vinylcyclopropanes,[4] which represent partial structures within **1**, react slowly to produce [2 + 2] cycloadducts or "ene" products. In order to account for the unusual reactivity of **1** with PTAD, a concerted cycloaddition mechanism involving interaction of the four π and two C_2-C_3 σ electrons of **1** with the two π electrons of PTAD, as illustrated in **2**, was proposed.[2] Subsequent stereochemical studies were fully consistent with the process represented in **2**.[5] We wish now to report the results of a kinetic study of the reaction of substituted alkenylidenecyclopropanes with PTAD, and an analysis of the kinetic and product distribution data in terms of ionization potentials and AO coefficients in the HOMO's as determined by photoelectron (PE) spectroscopic studies and CNDO calcula-