A Unified Description of Linear and Nonlinear Polarization in Organic Polymethine Dyes

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An internal or external electric field F can drive the chemical structure, bond order alternation, and electronic structure of linear polymethine dyes from a neutral, bond-alternated, polyene-like structure, through a cyanine-like structure, and ultimately to a zwitterionic (charge-separated) bond-alternated structure. As the structure evolves under the influence of F, the linear polarizability α, the first hyperpolarizability β, and the second hyperpolarizability γ are seen to be derivatives, with respect to F, of their next lower order polarization (for α) or polarizability (for β and γ). These derivative relations provide a unified picture of the dependence of the polarizability and hyperpolarizabilities on the structure in linear polymethine dyes. In addition, they allow for predictions of structure-property relations of higher order hyperpolarizabilities.

Since the discovery of synthetic dyes in the 1800s, chemists and physicists have been attempting to understand the relation between chemical structure, electronic structure (*1–3*), linear optical properties, and linear polarizability of organic molecules. Over the past 20 years, much attention has also been paid to hyperpolarizabilities (*4–6*). This interest in understanding structure-property relations for molecular hyperpolarizabilities stems from the realization that the nonlinear optical effects associated with these hyperpolarizabilities, including frequency generation, electro-optical switching, and all optical switching, can be used for a variety of photonic applications (*7–9*). To a great extent, the structure-property relations for the linear polarizability α, the first hyperpolarizability β, and the second hyperpolarizability γ have been treated separately and as somewhat unrelated. It was realized that a large linear polarizability was a necessary but, as we have shown (*10–12*), not sufficient requirement to obtain large hyperpolarizabilities. In addition, Garito and others have recently suggested that donor-acceptor polyenes with significant β could have enhanced γ relative to centrosymmetric unsubstituted polyenes of similar conjugation length (*13–16*). However, a unified description of linear and nonlinear polarizability is still lacking. In an attempt to develop such a description, we have recently shown (*16*) that the polarizabilities, α, β, and γ, of linear polymethine dyes can be correlated with a single chemically relevant parameter, bond length alternation (BLA) [or a closely related parameter, the π-bond order alternation (BOA) (*17*)].

For linear polymethine dyes, BOA can be related to the mixing of two limiting resonance structures, one of which is neutral and the other of which exhibits a high degree of charge separation (Fig. 1). Thus, the structure and consequently the polarizabilities will largely be determined by the relative energetics of the two forms. The charge-separated form can be stabilized chemically by (i) the tuning of the Coulomb potential of the end groups (that is, donor-acceptor strength); (ii) the molecular topology (that is, by gain of aromatic stabilization energy upon charge separation); and (iii) solvent-mediated polarization (that is, where a more polar solvent can stabilize charge separation). Although each of these forces, locally, may have different effects on the molecular and electronic structures, they correspond to first order to application of an effective electric field across a polarizable π-conjugated system. In this manner, the effective field (hereafter denoted **F**) induces charge separation and concomitant geometric modifications (*6, 16, 18, 19*). This realization leads to important conclusions regarding the relations among α, β, and γ as a function of **F**. In addition, because the ground-state structure is also determined by the magnitude of **F**, structure-property relations for nonlinear optics may also be inferred.

In this work, we demonstrate how a unified description of linear and nonlinear molecular polarizability can be gleaned by considering how the various polarizabilities appearing in the fundamental expansion of the induced dipole moment (μ_{ind}) as a function of a small perturbing field **E** (roughly 10^4 V cm^{-1}, as typically used in measurements) are related when the effect of the field **F** (which here is as large as 10^8 V cm^{-1}) on the ground-state structure is taken into account. Furthermore, experimental evidence will be presented that confirms our predictions and therefore provides strong evidence supporting our assertion that the effects of donor-acceptor strength, topology, and solvent stabilization are all analogous to that of applying an electric field across a molecule.

The molecular polarizabilities are defined by a Taylor series expansion of the

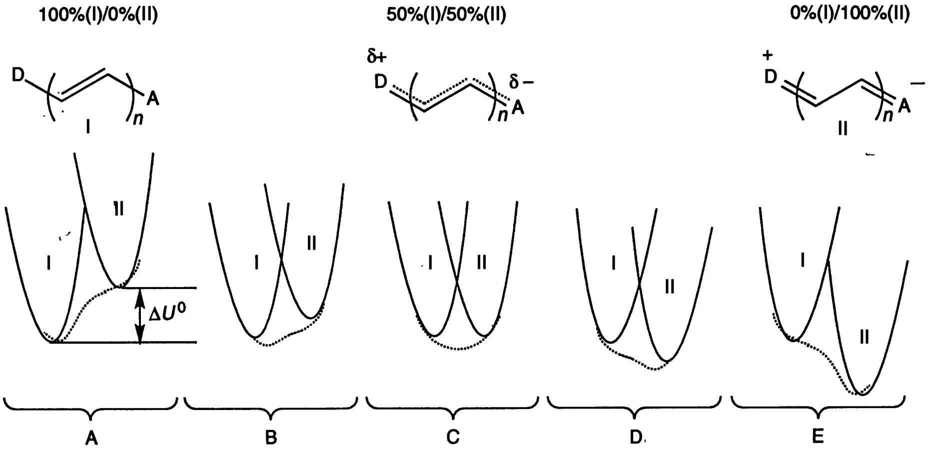

Fig. 1. Definition of regions (A through E) of BOA correlated with the percentage contribution of neutral (form I) and charge-separated (form II) resonance structures to the ground state. This diagram illustrates the evolution of the structure from neutral polyene-like, to polar cyanine-like, to very polar charge-separated polyene-like and correlates these structures with energy differences, ΔU^0, between potential wells for the neutral and charge-separated forms.

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total dipole moment in the small perturbing field **E** (*20*). Taking the field **F** into account, we have

$$\mu(\mathbf{F},\mathbf{E}) = \mu_0(\mathbf{F}) + \alpha_0(\mathbf{F})\mathbf{E} + \frac{1}{2!}\beta_0(\mathbf{F})\mathbf{E}^2 + \frac{1}{3!}\gamma_0(\mathbf{F})\mathbf{E}^3 + \frac{1}{4!}\delta_0(\mathbf{F})\mathbf{E}^4 + \cdots \qquad (1)$$

The static polarizabilities at a given value of **F**, as expansion parameters of the induced dipole moment, are related to derivatives, with respect to **E**, of the dipole moment or the $(n-1)$th order polarizability

$$\alpha_0(\mathbf{F}) = \left.\frac{\partial\mu(\mathbf{F})}{\partial\mathbf{E}}\right|_{\mathbf{E}\to 0}$$

$$\beta_0(\mathbf{F}) = \left.\frac{\partial^2\mu(\mathbf{F})}{\partial\mathbf{E}^2}\right|_{\mathbf{E}\to 0} = \left.\frac{\partial\alpha(\mathbf{F})}{\partial\mathbf{E}}\right|_{\mathbf{E}\to 0}$$

$$\gamma_0(\mathbf{F}) = \left.\frac{\partial^3\mu(\mathbf{F})}{\partial\mathbf{E}^3}\right|_{\mathbf{E}\to 0} = \left.\frac{\partial\beta(\mathbf{F})}{\partial\mathbf{E}}\right|_{\mathbf{E}\to 0} \qquad (2)$$

The mixing of the zero-order neutral (form I in Fig. 1) and charge-separated (form II in Fig. 1) resonance structures that largely control the structure and electronic properties of the ground state of the molecule depends on the energy difference between the zero-order states, $\Delta U^0 = U_{CT} - U_N$ [where U_{CT} is the energy of the charge-transfer state and U_N is the energy of the neutral state (Fig. 1); it is also related to the interaction matrix element coupling the states]. As noted above, the energy difference between the two zero-order states depends on (i) the donor and acceptor strength, (ii) the difference in the bridge π-electronic energy in the two forms, and (iii) the magnitude of the dipolar stabilization energy attributed to the reaction field of the medium. These energetic terms dictate the equilibrium ground-state structure and therefore the value of BOA, as well as the various polarizabilities (*16, 18, 19*).

To the extent that these factors result in a simple shift in the electronic energy difference of the two forms, we may view the shift as equivalent to a dipolar interaction energy and could consider the effect a result of the presence of an effective static electric field, **F**. This effective electric field induces a relaxation of the molecule to an equilibrium position on a BLA (or BOA) distortion coordinate (*16, 18, 19*). The linear and nonlinear polarizabilities, that is, the various order derivatives of μ_{ind} with respect to **E**, are then evaluated at the static effective perturbing field, **F**, that determines the equilibrium structure, BLA (or BOA). Because the Taylor series expansion of μ_{ind} with respect to **E** holds at each value of **F**, the derivative relations between the nonlinear polarizabilities are expected to hold as a function of **F**; that is

$$\alpha_0(\mathbf{F}) = \frac{\partial\mu_0(\mathbf{F})}{\partial\mathbf{F}}$$

$$\beta_0(\mathbf{F}) = \frac{\partial\alpha_0(\mathbf{F})}{\partial\mathbf{F}}$$

$$\gamma_0(\mathbf{F}) = \frac{\partial\beta_0(\mathbf{F})}{\partial\mathbf{F}}$$

$$\delta_0(\mathbf{F}) = \frac{\partial\gamma_0(\mathbf{F})}{\partial\mathbf{F}} \qquad (3)$$

To illustrate these derivative relations, we performed semiempirical INDO (intermediate neglect of differential overlap) calculations on $(CH_3)_2N\text{–}(CH{=}CH)_4\text{–}CHO$, in the presence of an external electric field **F**, applied along the long axis of the molecule (*18*). At each field strength, the geometry was optimized and a value of BOA was determined (Fig. 2A). The magnitude of **F** tunes the degree of mixing of the two canonical resonance forms. We calculated electronic states using configuration interaction with full single and limited double configuration excitations. We then evaluated hyperpolarizabilities using the sum over states approach derived from perturbation theory (*21*); the 30 lowest energy states were used to obtain converged values. We also numerically differentiated μ, α, and β with respect to **F** [thus, for example $\alpha_0(\mathbf{F}) \approx \Delta\mu_0(\mathbf{F})/\Delta\mathbf{F}$]. Because BOA is a function of **F** (Fig. 2A), we plotted results versus BOA; in this way, the structure-property relations predicted directly from the INDO calculations and those from the derivative curves could be compared and correlated with molecular structure (that is, BOA). As seen in Fig. 2, B through E, there is good agreement (in terms of both shape and peak positions as well as order of magnitude) between the numerical derivative of μ, α, and β with respect to **F** and its higher

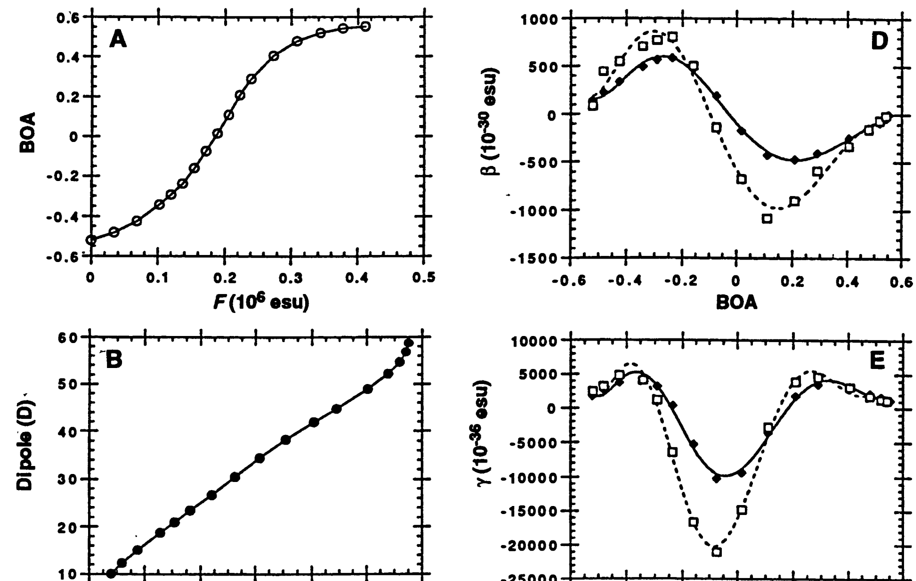


Fig. 2. Plots of (**A**) BOA versus the magnitude of **F**; (**B**) μ_0(**F**) versus BOA; (**C**) $\Delta\mu_0$(**F**)/Δ**F** versus BOA (open squares joined by dotted line) and α_0(**F**) versus BOA (filled diamonds joined by solid line); (**D**) $\Delta\alpha_0$(**F**)/Δ**F** versus BOA (open squares joined by dotted line) and β_0(**F**) versus BOA (filled diamonds joined by solid line); (**E**) $\Delta\beta_0$(**F**)/Δ**F** versus BOA (open squares joined by dotted line) and γ_0(**F**) versus BOA (filled diamonds joined by solid line); and (**F**) $\Delta\gamma_0$(**F**)/Δ**F** versus BOA; esu, electrostatic unit. The differences in magnitudes between the dotted and solid curves could largely result from limited number of points available for numerical differentiation; thus, the dotted curves are only rough approximations of the derivatives of the lower order polarizability.

order polarizability when they are both plotted versus BOA. These results allow us to predict that the third hyperpolarizability, δ, as a function of BOA will look like the derivative of γ with respect to **F** (Fig. 2F).

In an attempt to gain experimental evidence for the proposed relations, we examined molecules that spanned a wide range of polarization. We classify the molecules, qualitatively, on the basis of the degree of mixing between the neutral and charge-separated forms (Fig. 1), where approximately 100% neutral/0% charge-separated is defined as region A and the reverse is defined as region E; 50% neutral/50% charge-separated is defined as region C and corresponds to a cyanine-like molecule. Region B simply bridges regions A and C; likewise, region D bridges regions C and E (Fig. 1) (*12*). We used solvent polarity to fine-tune positions within the regions (with more polar solvents increasing the contribution of the charge-separated form) (*10–12*). The molecules we examined are shown in Fig. 3, and our assignment of these molecules to these regions is based on data derived from Raman, ultraviolet-visible, and ^{1}H nuclear magnetic resonance spectroscopies and x-ray crystallography (*11, 12, 22*).

With these molecules, we sought to map out the dispersion-corrected (*23*) $\beta(0)$ versus γ relations for given structures in the various regions. We therefore obtained values of $\mu\beta(0)$ for the molecules by electric field–induced second harmonic generation (EFISH) (*23–26*), as described earlier (*12*), and measurements of γ by third harmonic generation, in the manner described earlier for compounds 1 and 2 in Fig. 3 (*11, 22*). It should be noted that EFISH gives a direct measure of the $\mu\beta$ product, and the determination of μ introduces the greatest inaccuracy in the determination of β. Accordingly, we decided to compare the dispersion-corrected values of $\mu\beta$ [$\mu\beta(0)$] with γ. Because μ increases monotonically from region A to region E, the positive (negative) peaks of the $\mu\beta$ curve will be shifted toward region C (E), relative to the peak or peaks of the β curve. Nonetheless, given the uncertainties in the measurements and our desire to examine gross features of the curves, we believe that significant insight can be derived from these comparisons. In general, the critical points we seek to check are the regions in which β exhibits positive or negative peaks and where γ is expected to be zero. Also, where β is zero, γ is predicted to be negatively peaked (Fig. 2E). In fact, the values in Table 1 provide remarkably good confirmation of our predictions. In particular, for molecule 2, $\mu\beta$ peaks where γ changes sign from positive to negative. Likewise, for compounds 3 and 4, which fall in region C, when $\mu\beta$ changes sign, γ exhibits a negative peak. For compounds 5 and 6, which fall in regions C/D and D/E, respectively, the $\mu\beta$ peak occurs roughly where γ changes sign from negative

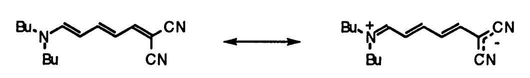
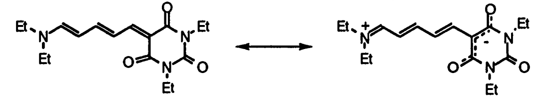
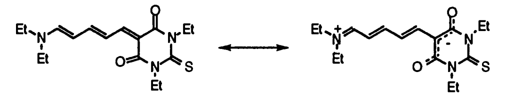
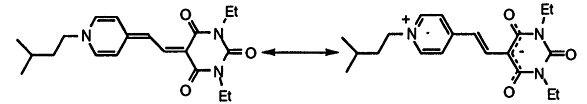
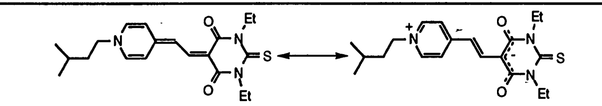
Compound	Resonance structures of compounds	BOA region
1		A
2		B
3		B/C
4		C
5		C/D
6		D/E

Fig. 3. Limiting resonance structures and numbering scheme for model donor-acceptor polyene compounds assigned to regions A through E; Et, ethyl; Bu, butyl.

Table 1. Top entries are $\mu\beta(0)$ values (in units of 10^{-48} esu), taken from (*12*). The estimated precision in $\mu\beta(0)$ is ±15%. Bottom entries are γ values (in units of 10^{-36} esu); values for compounds **1** and **2** are taken from (*11*). The estimated precision in γ is ±15%. Solvent polarity increases from left to right. The solvent polarities according to the normalized ET_{30} scale (which ranges from a value of 1 in water to a value of 0 in tetramethylsilane) are given in parentheses below the solvent (*28*).

Compound	Solvent								BOA region
	CCl_4 (0.053)	C_6H_6 (0.111)	Dioxane (0.164)	$CHCl_3$ (0.259)	CH_2Cl_2 (0.309)	CH_3CN (0.456)	CH_3NO_2 (0.482)	CH_3OH (0.762)	
1	236	213		247	263	268	327		
			40	95	105	113	113	73	A
2	245	255		281	238	162	136		
	40	15	−25	−42	−50	−120	−117	−135	B
3	272	137		133	94	74	−43		
		−20	−100	−135	−145	−205	−220	−166	B/C
4	177	168		−14	−38	−155	−203		
		−85	−170	−195	−175	−130	−125	−10	C
5		−117		−248	−276		−240		
			−25	15	30	79	73	150	C/D
6				−386	−500	−374	−247		
				130	167	228	227	291	D/E

to positive (for 6, γ is already positive where $\mu\beta$ exhibits a negative peak; the deviation here may be, at least in part, attributable to the fact that we are comparing $\mu\beta$ with γ, as noted above).

The theoretical study provides strong evidence that, as a function of **F**, α, β, and γ are related by derivatives. Because the BOA is also determined by **F**, we can relate the derivatives back to chemical structure. In order for these derivative relations to hold in the experiments described above, it is necessary to treat donor-acceptor strength, topology, and solvent stabilization as analogous to application of an effective electric field across a conjugated π-system. Thus, of fundamental importance to our basic understanding of the structure of molecules, the derivative relations demonstrated here provide strong support for the validity of this "effective electric field" concept, as applied to linear polymethine dyes. Still an open question is how well the "effective electric field" approximation and therefore the derivative relations will apply to two-dimensional molecules or to molecules with more extended conjugation. In addition, we demonstrated, contrary to some previous assessments (*27*), that γ will be roughly zero when β is optimized. The existence of molecules with negative γ, measured well below the three-photon resonance frequency (a phenomenon that has been a subject of controversy in the nonlinear optics community) is a natural outcome of α peaking at zero BOA (a result that can be derived from simple free electron calculations) because $\partial^2\alpha/\partial \mathbf{F}^2$ is clearly negative at this point. Furthermore, predictions were made for δ as a function of molecular structure (BOA or BLA).

These results thus provide a unified picture of linear and nonlinear optical properties of linear conjugated molecules that were heretofore often treated separately. We believe that our understanding of the relation between molecular structure and β and γ has progressed to the point where the measurements of these hyperpolarizabilities can themselves be used to provide detailed insight into the chemical structure (in particular, regarding mixing of various charge-transfer resonance forms) of linear polymethine molecules.

REFERENCES AND NOTES

1. S. Dähne, *Science* **199**, 1163 (1978).
2. J. Fabian and H. Hartmann, in *Light Absorption by Organic Colorants*, K. Hafner, Ed. (Reactivity and Structure Concepts in Organic Chemistry Series, Springer-Verlag, Berlin, 1980), vol. 12.
3. J. Griffiths, *Color and Constitution of Organic Molecules* (Academic Press, London, 1976).
4. K. C. Rustagi and J. Ducuing, *Opt. Commun.* **10**, 258 (1974).
5. J. L. Oudar and D. S. Chemla, *J. Chem. Phys.* **66**, 2664 (1977).
6. ——, *Opt. Commun.* **13**, 164 (1975).
7. P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers* (Wiley, New York, 1991).
8. S. R. Marder, J. E. Sohn, G. D. Stucky, Eds., *Materials for Nonlinear Optics: Chemical Perspectives* (American Chemical Society, Washington, DC, 1991), vol. 455.
9. J.-L. Brédas, C. Adant, P. Tackx, A. Persoons, B. M. Pierce, *Chem. Rev.* **94**, 243 (1994).
10. S. R. Marder, D. N. Beratan, L.-T. Cheng, *Science* **252**, 103 (1991).
11. S. R. Marder *et al.*, *ibid.* **261**, 186 (1993).
12. G. Bourhill *et al.*, *J. Am. Chem. Soc.* **116**, 2619 (1994).
13. A. F. Garito, J. R. Heflin, K. Y. Wong, O. Zamani-Khamiri, in *Organic Materials for Non-linear Optics: Royal Society of Chemistry Special Publication No. 69*, R. A. Hann and D. Bloor, Eds. (Royal Society of Chemistry, Burlington House, London, 1989), pp. 16–27.
14. M. G. Kuzyk and C. W. Dirk, *Phys. Rev. A* **41**, 5098 (1990).
15. B. M. Pierce, *Proc. SPIE* **1560**, 148 (1991).
16. C. B. Gorman and S. R. Marder, *Proc. Natl. Acad. Sci. U.S.A.* **90**, 11297 (1993).
17. L. Salem, *The Molecular Orbital Theory of Conjugated Systems* (Benjamin, New York, 1966).
18. F. Meyers, S. R. Marder, B. M. Pierce, J.-L. Brédas, in preparation.
19. D. Lu, G. Chen, W. A. Goddard III, J. W. Perry, in preparation.
20. A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).
21. B. J. Orr and J. F. Ward, *Mol. Phys.* **20**, 513 (1971).
22. G. Bourhill *et al.*, *Proc. SPIE* **1853**, 208 (1993).
23. J. L. Oudar and H. L. Person, *Opt. Commun.* **15**, 258 (1975).
24. B. F. Levine and C. G. Bethea, *Appl. Phys. Lett.* **24**, 445 (1974).
25. K. D. Singer and A. F. Garito, *J. Chem. Phys.* **75**, 3572 (1981).
26. L.-T. Cheng *et al.*, *J. Phys. Chem.* **95**, 10631 (1991).
27. C. W. Dirk, L.-T. Cheng, M. Kuzyk, *Int. J. Quant. Chem.* **43**, 27 (1992).
28. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry* (VCH, Weinheim, Germany, ed. 2, 1988).
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A Formation Mechanism for Catalytically Grown Helix-Shaped Graphite Nanotubes

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The concept of a spatial-velocity hodograph is introduced to describe quantitatively the extrusion of a carbon tubule from a catalytic particle. The conditions under which a continuous tubular surface can be generated are discussed in terms of this hodograph, the shape of which determines the geometry of the initial nanotube. The model is consistent with all observed tubular shapes and explains why the formation process induces stresses that may lead to "spontaneous" plastic deformation of the tubule. This result is due to the violation of the continuity condition, that is, to the mismatch between the extrusion velocity by the catalytic particle, required to generate a continuous tubular surface, and the rate of carbon deposition.

The formation of coiled carbon fibers and their morphology have been described recently in a number of papers (*1–10*). The fibers were found to be hollow tubes consisting of concentric cylindrical graphene sheets. They are prepared by the high-temperature (600° to 700°C) catalytic decomposition of organic vapors such as acetylene or benzene on a finely divided metallic catalyst such as Co, Fe, or Ni. The tubules can adopt various shapes such as straight, curved, planar-spiral, and helix, often with a remarkably constant pitch. It is generally accepted that the tubules grow by the extrusion of carbon, dissolved in a metallic catalyst particle that is oversaturated in carbon at one part of the surface. The most detailed description of the growth process was given by Baker (*1*), who emphasized the chemical aspects and treated only the case of straight cylindrical tubes.

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